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RESEARCH PAPER RP881

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ARC AND SPARK SPECTRA OF COLUMBIUM

By William F. Meggers and Arthur S. King *

ABSTRACT

A new description of conventional arc and spark spectra of columbium (niobium) in the wave-length range 2100 to 12000 A has been completed. Wave-length measurements are presented for 5700 lines, the majority to 7 significant figures, with an average probable error less than 0.005 A. Intensity comparisons of lines from the two types of sources permit an unambiguous separation of Cb I, Cb II, and Cb III or Cb IV spectra. These data should facilitate spectroscopic identification and analysis of columbium, and serve as a basis for further study of spectral structures, Zeeman effects, and hyperfine structures.

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I. INTRODUCTION

The literature on spectra of columbium (niobium) from 1868 to 1933 is listed and discussed in Kayser's Handbuch der Spectroscopie.[1] Since the total number of papers dealing in any way with the optical spectra of this element is less than 30, it can properly be said that columbium has been neglected. No comprehensive and accurate measurements of wave lengths have been published for columbium in the past 25 years, and Kayser, who quotes all available data for these spectra, states "Die Tabelle von Nb (Cb) ist weit davon entfernt, vollständig zu sein, obwohl die Zahl der gemessenen Bogen- und Funkenlinien etwa 4500 beträgt."

A dozen years ago one of the present authors became interested in a term analysis of columbium spectra, and with the aid of data then available succeeded in finding a few multiplets in the Cb I[2] and Cb II[3] spectra. The impossibility of extending such analyses without improved and additional descriptive material was responsible for investigation of furnace spectra,[4] for remeasurement of the arc and spark spectra,[5] and for further observations of Zeeman effects. These new data have greatly advanced the term analyses,[6] and remeasurement

* Mt. Wilson Observatory, Pasadena, Calif.

[1] H. Kayser, Handbuch der Spectroscopie **6**, 128–159 (S. Hirzel, Leipzig, 1912); **7**, 1397–1446 (S. Hirzel, Leipzig, 1934).
[2] W. F. Meggers, J. Wash. Acad. Sci. **14**, 442 (1924).
[3] W. F. Meggers and C. C. Kiess, J. Opt. Soc. Am. **12**, 417 (1926).
[4] A. S. King, Astrophys. J. **73**, 13 (1931).
[5] A. S. King and W. F. Meggers, Phys. Rev. [2], **37**, 226 (1931).
[6] W. F. Meggers and B. F. Scribner, NBS J. Research **14**, 629 (1935) RP793.

of the spectra now permits satisfactory spectroscopic identification and analysis of columbium.

Although discovered in 1801, columbium for more than a century remained a chemical curiosity, and has been one of the latest to find industrial application. Just recently, it has been given an important use in the steel industry. The metal when alloyed in moderate and economical proportions with the austenitic chromium-nickel steels inhibits intergranular corrosion, and is expected to give fresh impetus to industrial utilization.[7] A ton a day is now being refined and used for this purpose. Since this is likely to continue and since also the use of spectra for chemical identification and quantitative analysis is developing rapidly, it will not be long before practical spectroscopists will be wishing for a satisfactory description of columbium spectra. It is primarily in anticipation of such demand that we offer the following table of arc and spark spectra, which may also serve as a basis for further work on term analysis, Zeeman effects, hyperfine structure, etc.

II. EXPERIMENTAL

All former observers of columbium spectra were forced to use more or less impure salts and carbons, because metal of high purity has been produced only recently. The electrodes used for the production of spectra herein to be described were solid rods of columbium metal about 1 cm in diameter, kindly presented for spectroscopic investigations by C. W. Balke in 1929. A second pair of electrodes was generously supplied by Balke in 1931. These columbium rods contained a considerable amount of tin and a trace of iron but were otherwise spectroscopically pure. It is remarkable that none of the observed spectral lines could be identified with the chemically homologous elements, vanadium and tantalum. Most of the known lines of tin appeared on our spectrograms, but they were removed from the final list. The strongest lines of iron showed faintly in the columbium spectrograms and were not measured except as wave-length standards.

The arcs were operated with direct current of 5 or 6 amperes, the applied potential being 220 volts. The sparks were produced by supplying transformers with 50 or 60 cycle alternating current and connecting the electrodes to the secondary (10,000 or 40,000 volt) terminals, with mica or glass condensers in parallel.

For recording these spectra, special photographic plates were selected for different spectral regions. The middle portion (2700 to 6700 A) was photographed in 1930 on Eastman and on Ilford plates. Hilger Schumann plates were used in the ultraviolet, and observation of the infrared was improved and extended from time to time by applying new types of sensitized plates supplied by the Eastman Kodak Co.[8] The entire range now accessible to photography with large-scale spectrographs in air has thus been studied. Description and analysis of these spectra are being extended in the extreme ultraviolet by R. J. Lang,[9] employing vacuum spectrographs.

In making a new description of columbium spectra, we aimed to strive for satisfactory precision of wave-length measurements, and sufficiently accurate estimates of relative intensities to permit differ-

[7] F. M. Becket and R. Franks, Trans. Am. Inst. Mining Met. Engrs., Iron and Steel Div. 113, 143 (1934).
[8] Photographic Plates for Use in Spectroscopy and Astronomy (Eastman Kodak Co., March 1935).
[9] R. J. Lang, Zeeman Verhandelingen, p. 44 (1935).

entiation of ionization stages. To obtain the first objective in such complex spectra as those characteristic of columbium, large spectrographs with adequate resolving power and freedom from false spectra or ghosts must be employed. In this particular case, however, the resolving power should not be so great as to cause confusion of hyperfine structure with ordinary line structure neglecting nuclear effects. The spectrographs actually employed in these observations are described in table 1.

TABLE 1.—*Spectrographs used for description of* Cb *spectra*

Spectral region	Spectrograph	Maker	Dispersion
A			A/mm
2100 to 2700	NBS quartz prism	Adam Hilger	0.4–1.1
2600 to 5400	MW concave grating 2d order	Anderson	1.8
5300 to 7700	MW concave grating; 1st order	do	3.7
6700 to 9000	NBS concave grating; 1st order	Rowland	3.5
8800 to 10000	do	Wood	5.1
9000 to 12000	do	Anderson	10.2

The Hilger quartz spectrograph is an efficient autocollimating instrument of about 3-m focal length so constructed that the dispersion and resolving power are equivalent to those obtained from three 60° prisms, each with 20 cm base thickness.

The Mount Wilson concave-grating spectrograph is the vertical adaptation of the Rowland mounting described in another paper.[10] This grating has 15,000 lines per inch and a radius of 15 feet.

Each of the National Bureau of Standards gratings has a radius of curvature of 21.5 feet, but the number of lines per inch is 20,000, 15,000, and 7,500 in the order listed. Each performs stigmatically since the grating is illuminated with a (stainless steel) mirror having the slit at its principal focus, and observations are made on or near the normal to the grating.[11] The NBS Rowland grating has practically the same scale and power as the MW Anderson grating, but its "Rowland ghosts" are so strong in the second order that it is unsatisfactory for use on fully exposed complex spectra. For this reason, after the work on furnace spectra of columbium had shown the superiority of the MW grating, the authors arranged this cooperative program to produce a new description of columbium spectra. A large number of spectrograms, covering the visible and near ultraviolet, were made at Mount Wilson, and supplemented by others secured at the National Bureau of Standards for description of the infrared and shorter ultraviolet. The best spectrograms were selected for measurement at the National Bureau of Standards, where all the actual measurements and calculations were performed. The authors are indebted to B. F. Scribner for executing a considerable portion of the calculations.

To facilitate intensity comparisons most of the spectrograms record arc and spark spectra of columbium on the same plate, with a comparison spectrum of iron between. Other spectrograms of arc or spark alone (each with iron comparison) were prepared so that wave-

[10] A. S. King, Astrophys. J. **40**, 19 (1914).
[11] W. F. Meggers and K. Burns, BS Sci. Pap. **18**, 191 (1922).

length measurements could be made of each without bias on account of the other. It is well known that lines enhanced in a high-potential condensed spark are, in general, more diffuse than arc lines, and almost invariably appear to be displaced toward longer waves. These phenomena, ascribed to Stark effect, make it difficult to determine the true wave lengths. For spark lines which appear in the arc, we have decided to publish only the values derived from arc spectra. Corresponding values from spark spectrograms are larger by various amounts up to 0.02 or 0.03 A, the difference usually increasing with degree of enhancement of the line. Unfortunately, it is not possible to give the true values of lines which appear only in the spark, but it may be assumed that the majority of them are at least 0.02 to 0.03 A; too large on account of Stark effect.

Each spectrogram was measured in both directions and each line finally retained was observed on two to nine plates. Altogether this labor of measuring columbium spectra relative to iron standards involved more than 100,000 microscopic bisections of spectral-line images. For purposes of calculation each spectrogram was divided into parts so that the maximum deviations from standards never exceeded ± 0.02 A. Prism spectrograms were reduced with Hartman's interpolation formula,[12] while grating spectrograms were assumed to have constant dispersion over short intervals.

The standards employed were the international iron arc secondary standards of wave length.[13] supplemented in the ultraviolet by observed and computed values published by Burns and Walters.[14] Since these standards have probable errors or one or more units in the seventh figure, it may be questioned if it is legitimate to retain more than six figures in comparison measurements. In the present case, we have kept the seventh figure only when the average deviation from the arithmetical mean of two or more observations is less than 0.005 A. Actual computation of probable errors for random lines with four observations on second order grating spectrograms indicate an average probable error of ± 0.002 A. A practical test of these wave lengths was presented in a paper on multiplets and terms in the first two spectra of columbium,[15] in which it was shown that the average deviations of an observed wave number from the corresponding term combination is ± 0.02 cm^{-1} for 413 classified Cb I lines, and ±0.04 cm^{-1} for 255 classified Cb II lines. If the average wave length of each group is considered, it will be seen that in each case the deviations correspond to wave-length errors less than ±0.005 A. It is perhaps surprising that the fit should be so good in view of the fact that many lines have hyperfine structure widths of 0.2 to 0.5 A. The width of 8320.93 A exceeds 1.0 A. For all unresolved complex lines we give values corresponding to the centers of gravity only, but these values usually represent the mean of edge measurements in the case of the wider lines.

[12] W. F. Meggers, Dictionary of Applied Physics 4, 890 (1923).
[13] Trans. Int. Astron. Union 3, 86 (1928).
[14] K. Burns and F. M. Walters, Jr., Pub. Allegheny Obs. 6, 159 (1929).
[15] W. F. Meggers and B. F. Scribner, NBS J. Research 14, 629 (1935) RP793.

III. RESULTS

Our results for arc and spark spectra of columbium from 2100 to 12000 A are presented in table 2, which contains 5700 lines. The lines are represented by wave lengths followed by estimated relative intensities of arc and spark images, and descriptive symbols. An effort was made to maintain a fairly uniform and expanded scale of intensities comparable with that adopted in the description of furnace spectra.[16] Toward 2100 A the arc intensities may be too large for lines characteristic of ionized atoms on account of projecting the image of a short arc with a simple quartz lens, thus bringing light from the electrodes into the spectrograph. In general, however, a comparison of intensities from arc and spark sources differentiates without ambiguity Cb I, Cb II, and Cb III spectra. Lines from neutral columbium atoms, yielding the Cb I spectrum, can be recognized by outstanding strength in the arc. Lines from singly ionized atoms constitute the Cb II spectrum, and although many of these appear in the arc, they are generally enhanced in the spark, the degree of enhancement being proportional to the excitation energy required to produce them. Many Cb II lines do not appear in the arc at all, and are more or less hazy and unsymmetrical in the spark. A small proportion of the lines excited only in the condensed spark are enhanced at the electrodes. It is fairly certain that all lines marked "e" in table 2 belong to doubly or to trebly ionized atoms, but our observations do not permit a differentiation between Cb III and Cb IV spectra. A study of the relative intensities of these lines when self-inductance is introduced in the discharge circuit might lead to a separation of these higher ionization stages.

Columbium spectra are characterized by an exceptional richness in number and variety of lines. Throughout the ultraviolet the average line density is 2 per angstrom unit, and in some regions as large as 6 lines per A. In the visible and infrared, where the line density appears to be smaller, many atomic lines may be masked by molecular spectra (presumably due to CbO), which are very prominent in the conventional atmospheric sources. A few faint band heads are recognized in the blue, stronger ones in the orange, but the most intense ones are found in the red and infrared. Each band head is accompanied by a dense background of partially resolved rotation structure, among which it is practically impossible to recognize fainter atomic lines. Although these molecular spectra are not so intense in spark spectrograms, if the latter are exposed sufficiently to record all arc lines, the bands are developed with equal intensity. Perhaps these molecular spectra can be eliminated in vacuum sources or in Paschen hollow-cathode discharges. Practically all details of molecular spectra except band heads have been omitted in table 2.

A striking feature of columbium spectra, first mentioned[17] in 1931, is the hyperfine structure. Although almost none of this is resolved by the spectrographs employed in this work, a large proportion of the spectral-line images appear to be sharp-edged and flat-topped, indicating that the images are formed by two or more close components. In some patterns incipient resolution was suggested on one side or the other, giving the impression that they

[16] A. S. King, Astrophys. J. **73**, 13 (1931).
[17] A. S. King, Astrophys. J. **73**, 13 (1931).

might all be so-called "flag-patterns" in which both intensity and separation of components decrease regularly in one direction or the other. Except for a symbol "*c*" denoting complex hyperfine structure suggested by our spectrograms, we have omitted further details of these phenomena. In some instances the symbols "*d*" and "*h*" may also represent hyperfine structure, since it is often difficult to make absolute distinctions of this kind. This hyperfine structure of columbium lines has been studied in some detail by Ballard,[18] who deduces from it a nuclear spin moment of $I=9/2$ for columbium atoms.

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)

c=Complex, hyperfine structure (*hfs*).
d=Double, may be *hfs*.
e=Enhanced at electrode.
h=Hazy.
H=Very hazy.
l=Shaded or displaced to longer waves.
s=Shaded or displaced to shorter waves.
B=Band head.
p=Part of band structure.
r=Narrow self-reversal.
R=Wide self-reversal.

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
2102.13	2	—	2137.055	15	20	2158.135	20	10
2103.59	20	10	2137.546	20	40	2160.269	50	100
2107.267	40	30	2138.42	3	4*h*	2160.340	20	40
2108.23	2	1	2138.552	2	—	2161.54	5	—
2108.34	2	1	2138.89	5	6	2162.63	2	1
2109.428	100	150	2140.39	15	10	2163.076	10	5
2110.05	10	10	2140.48	3	1	2163.821	5	3
2110.96	2	1	2142.02	5	5	2164.26	2	2*h*
2111.17	2	1	2142.52	2	1	2166.77	5	—
2112.30	—	6*hc*	2142.91	6	5	2167.241	40	80
2113.034	50	50	2143.20	4	4	2168.188	4	2
2114.77	2	1	2143.64	1	—	2169.892	10	15*h*
2115.16	—	1*h*	2144.17	—	9*hc*	2170.718	4	8*h*
2116.387	10	5	2144.487	4	2	2171.03	1	—
2118.873	30	20	2144.79	4	2	2172.40	3	4
2119.06	5	5	2146.14	—	15*He*	2172.48	2	1
2119.63	3	1	2146.358	—	50*He*	2175.555	8	—
2119.98	2	1	2147.197	40	20	2175.844	30	40
2120.52	5	3	2148.650	30	10Sn?	2176.761	40	60
2121.63	—	6*hc*	2148.726	2	—	2176.986	2	—
2122.67	—	20*hc*	2149.03	5	5	2177.25	—	20*h*
2122.73	4	—	2149.539	30	20	2177.36	1	—
2124.33	5	5	2152.05	4	4	2178.07	3	—
2125.209	50	60	2152.57	1	1	2178.225	4	—
2126.541	50	60	2153.30	2	3	2180.670	10c	10c
2127.35	2	—	2153.556	3	1	2185.398	4	4
2128.12	2	1	2153.61	—	3*h*	2185.872	1c	2c
2128.21	2	1	2154.207	20	10	2187.036	—	3*h*
2129.00	2	1	2154.474	5	6	2188.138	—	6*h*
2129.69	3	2	2154.73	2	—	2188.944	7	—
2130.23	—	25*hc*	2154.91	1	1	2192.414	6	7
2131.181	50	60	2155.13	2	2*h*	2193.011	8	—
2132.03	1	—	2155.621	25	40*h*	2193.805	10	—
2132.83	7	6	2155.59	1	—	2195.660	—	2*H*
2133.17	2	1	2156.21	—	10*hc*	2195.74	4*h*	—
2133.67	3	1	2156.27	2	—	2195.77	—	15*h*
2134.492	20	15	2156.40	2	—	2195.83	3*h*	—
2134.710	30	40	2156.736	40	20	2196.39	—	20*h*
2134.952	15	20	2157.27	6	8*h*	2196.84	2	—
2135.32	1	—	2157.48	2	1	2198.33	—	1*H*

[18] S. S. Ballard, Phys. Rev. **46**, 806 (1934).

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
2199.04	1	2h	2237.496	80	100	2269.653	4	—
2199.603	5	8h	2238.14	1	2	2269.865	10	80h
2199.969	25	100h	2238.518	80c	1	2270.180	40	120h
2200.218	4	—	2240.31	—	60*He*	2270.65	—	2
2201.362	—	6h	2240.645	15	50*hl*	2272.730	40	80
2201.916	3	—	2241.011	2	15*hl*	2273.120	—	6h
2202.007	6	7	2241.855	8h	—	2273.566	60	120h
2203.170	5	6	2242.294	20	3	2273.91	—	100*He*
2203.555	3	—	2242.579	40	50*hl*	2274.128	50	100h
2203.637	60	150h	2242.958	20	—	2274.198	10	50h
2204.617	12	—	2244.184	—	50*He*	2274.770	9h	—
2205.230	2	—	2244.29	1	50*H*	2275.219	—	150*He*
2206.016	—	40*He*	2244.92	—	4h	2276.170	4	6
2206.639	1	4h	2245.15	1	2	2276.223	4h	—
2207.182	10	20h	2245.26	—	2	2276.361	3	3
2210.31	—	2h	2246.176	90c	1	2277.426	15	—
2210.442	6	—	2246.421	8c	—	2277.586	2	—
2210.534	15	40h	2246.500	2	15h	2278.320	—	4h
2210.622	7	—	2246.752	—	100*He*	2278.477	—	4h
2210.917	15	20h	2246.98	1	10h	2279.386	—	80*He*
2211.274	3	6h	2247.188	4	4	2279.414	2	—
2211.46	50c	—	2247.997	80	1	2280.450	40	50
2212.222	2	—	2248.282	2	60	2280.912	1	—
2212.927	—	3h	2248.84	—	50*He*	2281.136	7	20
2214.034	40c	—	2249.52	—	60*He*	2281.505	—	200*He*
2215.29	3	4	2250.005	2	6h	2281.830	5	80h
2215.54	30c	—	2250.308	100c	2	2283.004	100	200
2217.18	—	10*He*	2250.463	20	60*hl*	2283.377	4h	1
2217.24	4h	10*H*	2251.39	2h	—	2284.356	3	9h
2217.872	15	—	2251.51	4h	—	2284.41	—	70*He*
2218.357	3	—	2252.09	2	—	2285.223	40	60h
2219.163	3	5h	2252.210	25	200	2285.673	—	5h
2219.328	3	10*hl*	2252.623	4	15	2286.352	2	8h
2220.184	70c	2	2252.754	2	—	2286.749	1	15
2220.277	—	5h	2253.31	—	2h	2286.892	7	7
2220.417	—	4h	2253.802	8	—	2287.02	—	6*He*
2221.415	1	4	2254.564	150	2	2287.504	5h	—
2221.474	2	1	2254.953	20	40	2288.861	10	30h
2221.70	—	4*He*	2255.175	1	3h	2289.840	5h	—
2223.672	60c	—	2255.597	80	150	2290.289	6	6
2224.667	20	30*hl*	2255.791	5	—	2290.39	—	150*He*
2225.096	—	10*He*	2256.075	6	—	2291.383	8	6
2225.235	6	—	2257.537	10	40*hl*	2291.644	2	20h
2225.343	50	1	2257.886	160	2	2292.325	—	8*hl*
2225.547	3	5*hl*	2260.854	20	—	2293.145	2	6h
2226.927	15	—	2261.531	2	15h	2293.274	6	—
2227.280	10	—	2261.721	7	7h	2293.41	—	3*He*
2227.706	150c	3c	2262.132	15	60h	2293.926	12	40*hl*
2228.032	100c	2c	2262.34	1	2	2294.41	—	4*He*
2228.39	4	—	2263.219	4	12h	2294.484	2	—
2229.65	30	—	2263.312	8	10h	2294.71	—	5*He*
2229.716	30	100h	2264.074	5	3h	2294.983	6	50h
2230.74	1h	4h	2264.354	3	—	2295.681	100	250
2230.85	1h	8h	2264.556	20	120h	2295.972	6	8
2231.428	8	—	2265.217	4	—	2296.748	2	3h
2232.545	80c	1	2265.489	2	—	2297.611	15	50h
2233.172	9	—	2265.592	—	50*He*	2297.853	2	40h
2233.54	—	10h	2265.676	40	100*hl*	2298.385	8	10
2235.66	1	2h	2266.732	20	100*hl*	2298.602	7	5
2235.89	1	2h	2267.44	—	3*He*	2299.226	8	20h
2236.22	10	—	2268.287	2h	—	2300.295	6	—
2236.43	1	4h	2268.527	60h	100h	2300.339	10	30h
2236.724	20	40h	2268.59	3	—	2300.519	4	5h
2236.95	1	5h	2269.202	1	10h	2300.785	40	50
2237.30	—	10*hl*	2269.535	4	—	2300.854	8	—

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
2302.086	100	200	2335.322	15	20	2364.270	—	3h
2302.695	30	40	2335.620	6	30	2364.325	5h	—
2303.154	2	4	2336.410	7	—	2365.215	30	70
2304.26	1	—	2337.603	1	—	2365.305	3	4h
2304.363	—	7*He*	2337.744	20c	—	2365.624	2	20h
2304.77	—	40*He*	2338.091	—	40*He*	2365.745	1	10h
2305.29	3	—	2338.38	2	—	2365.940	3	—
2305.426	—	4h	2338.42	2	—	2666.198	1	20h
2305.975	4	—	2338.730	4	—	2366.715	1	—
2306.59	1	—	2339.58	—	4*H*	2367.367	—	5*H*
2307.477	3	3	2339.876	2	—	2368.64	3	—
2307.759	3	—	2340.025	2	20h	2368.860	15	—
2308.807	6	5	2340.149	8	—	2368.941	1	6h
2309.239	60	100	2340.277	10	—	2369.954	30	100
2309.742	3	4	2340.931	2	—	2370.732	—	4*H*
2309.93	—	15*H*	2341.152	3	—	2372.227	4c	8c
2310.313	2	8h	2342.852	1	4h	2372.730	4	50hc
2310.570	2	2	2343.103	1	3h	2373.074	3	—
2311.456	4	20h	2343.271	10	8	2373.967	4c	10c
2311.676	7	—	2343.66	—	3*H*	2374.167	1	8
2313.171	2	—	2344.075	3	?	2374.459	1	—
2313.31	—	200*H*	2344.12	—	15*He*	2374.924	2	—
2313.370	1	—	2344.517	15c	—	2376.398	30	100
2313.524	15	10	2344.640	8c	—	2377.989	2	15
2314.240	1	3h	2345.333	2	15h	2378.476	2	4
2314.359	4	—	2346.532	25	40	2378.935	2	—
2314.850	30	50	2346.679	10c	—	2379.122	—	5h
2315.173	20	15	2346.961	—	3	2380.148	1	10h
2316.271	3h	—	2347.111	—	1	2381.122	1	2
2316.929	6	15h	2348.639	—	5*H*	2381.717	4	4
2317.784	10	10h	2348.756	10c	—	2382.246	4	—
2318.180	—	3h	2349.217	—	40*He*	2382.79	—	1h
2318.432	5	—	2349.411	—	5h	2383.843	2	—
2319.589	15	25h	2350.034	6	—	2384.208	—	3*H*
2319.847	3	5h	2350.488	8	20h	2384.827	2	—
2320.238	25	20h	2350.710	2	—	2384.852	—	5h
2320.659	2	8h	2351.613	2	4	2385.251	2	10h
2321.271	—	3h	2351.677	4	—	2386.406	2	—
2321.489	4	—	2352.055	2	—	2387.101	20	30
2321.621	2	—	2352.131	3	—	2387.399	—	10*H*
2321.996	20	30h	2352.338	20	60h	2387.521	30	90
2322.992	8h	—	2352.837	30	60h	2388.269	20	40
2323.512	2	15h	2353.510	6	—	2390.080	2	—
2323.654	3	—	2353.765	2	4	2390.385	—	2
2323.884	1	—	2353.80	10	—	2390.454	4	—
2323.959	1	—	2354.040	15	50	2390.718	—	2h
2324.063	8	40h	2354.470	9	—	2391.912	5	20
2324.237	40	50h	2354.941	—	3h	2392.932	1	—
2324.409	1	3h	2355.533	—	20*He*	2393.110	2	—
2324.600	4	—	2355.680	8	6	2394.058	5	—
2325.504	2	6h	2356.005	10	30	2394.395	4	—
2326.221	5	30h	2356.290	15	40	2394.697	1	2
2326.964	3	—	2357.437	1	3	2395.329	20	40
2327.131	10	15h	2358.134	6	—	2395.824	1c	3c
2327.521	—	4h	2359.679	3	—	2396.310	—	3c
2328.028	3	5h	2360.302	20	70	2396.772	3c	2
2328.077	4	—	2360.794	2	—	2397.175	—	2
2328.222	5	—	2361.051	—	10*He*	2397.558	1	4c
2330.202	—	10*He*	2362.046	—	60*He*	2397.677	2	2
2331.224	2	—	2362.489	—	30*He*	2397.967	4	6h
2332.295	—	4h	2362.50	3	—	2398.484	30	120
2332.704	—	2	2363.062	4	—	2398.768	1	2
2332.896	10	10	2363.587	2	4	2399.718	5	—
2333.650	10	—	2363.716	2h	—	2400.054	2	—
2334.488	2	—	2363.852	4h	—	2400.910	5	—

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
2401.040	2	4	2427.627	2	—	2453.367	20	1
2401.272	—	4	2427.714	1	—	2453.853	8	15
2401.873	3	—	2428.047	3	—	2453.945	7	15
2402.339	8c	—	2428.096	3	—	2454.057	—	4*H*
2402.658	—	8*h*	2428.603	2	8*h*	2454.163	2	—
2403.107	4	—	2428.848	3	—	2454.376	—	4*h*.
2403.918	4	—	2428.880	—	20*He*	2454.592	1	—
2404.210	2	20*h*	2430.310	1	4*h*	2455.534	—	5*He*
2404.278	—	15*he*	2430.442	2	—	2455.872	3	—
2404.895	—	50*H*	2431.679	3c	30c	2456.676	3c	6c
2405.344	25c	50c	2432.321	5c	10c	2456.83	1	—
2405.576	2	—	2432.822	1c	8c	2456.999	—	400*He*
2405.850	30c	60c	2433.56	—	8*He*	2457.243	—	50*He*
2406.942	10	1	2433.680	10	—	2458.083	10	40*h*
2407.685	6	20*h*	2433.792	15	60*hl*	2458.310	—	8*He*
2408.056	2	—	2434.117	—	1	2458.575	5	—
2410.080	1	6*h*	2434.310	1	—	2459.290	1	—
2410.285	10c	20c	2434.391	1	—	2459.434	1	2
2410.792	3*h*	—	2434.662	—	3	2459.563	2	8*h*
2411.235	—	5*h*	2434.878	4*h*	—	2460.398	—	100*He*
2412.283	—	5*h*	2434.962	6	—	2461.174	4c	9c
2412.460	40	150*h*	2435.074	2	10*h*	2461.757	10	—
2412.645	5	—	2435.374	2	5*h*	2462.047	2	60
2412.805	1	30*hl*	2435.952	15	50*h*	2462.500	2c	4c
2413.936	—	200*hl*	2436.252	2	—	2462.889	20	1
2414.206	7	—	2436.329	12	2	2463.631	5	—
2414.485	—	150*hl*	2437.08	—	1	2463.732	—	10*He*
2414.762	2c	—	2437.161	9	1	2464.432	10	—
2414.876	—	6*H*	2437.411	20	50	2464.648	1	15*h*
2415.678	1	—	2437.721	—	15*He*	2465.199	—	4*h*
2415.955	5c	10c	2437.924	3	—	2465.709	2*h*	—
2416.169	15	30	2438.110	1	—	2466.318	10	—
2416.247	2	3*h*	2439.445	2	—	2466.563	2	9
2416.679	2	2	2439.715	3	—	2466.727	25	1
2416.994	40	150*h*	2440.392	5	—	2467.630	3	—
2417.157	—	20*hl*	2440.976	3	8	2468.035	—	2*h*
2417.323	8	15*h*	2441.021	2	—	2468.064	1	—
2418.05	2*h*	—	2441.224	—	2*H*	2468.734	—	60*He*
2418.168	2	—	2441.856	10c	30	2469.072	25	1
2418.490	3	—	2442.144	15	40	2469.403	—	50*He*
2418.687	30	150*h*	2442.677	7	40	2470.647	2	—
2418.792	4	—	2443.104	2	—	2471.25	1	—
2419.467	4	10*h*	2443.529	8	1	2471.318	5c	20c
2419.804	6	—	2443.718	2	2	2472.376	5	20
2419.976	5c	—	2444.479	3	10	2472.981	—	2*h*
2420.144	7	—	2444.856	—	3*h*	2473.752	2	—
2420.461	2	—	2445.066	20	2	2474.187	—	3*h*
2421.016	2	2	2445.172	1	—	2474.655	15	—
2421.914	—	150*H*	2445.402	2	2	2474.82	—	8*H*
2422.900	3	—	2445.832	—	30*H*	2475.881	—	50*He*
2422.976	1	2*h*	2445.913	1	—	2476.478	7	—
2423.064	—	3*H*	2446.080	—	20*He*	2477.379	50	150
2423.532	—	4*h*	2446.130	10	—	2477.720	1	—
2423.996	4	—	2446.439	—	30*He*	2477.936	5	20
2425.112	1	5*h*	2446.764	—	2	2478.283	20	60
2425.337	2	—	2447.413	4	—	2478.567	—	4*h*C?
2425.741	5	—	2447.966	8	15	2479.351	1	—
2426.128	—	4*h*	2448.258	2c	20c	2479.454	—	1
2426.243	1	5*h*	2450.069	1	5	2479.933	25	80
2426.637	6*h*	—	2450.250	3	10	2481.434	2	—
2426.794	—	50*Hl*	2450.433	7	12	2483.721	5	15
2426.957	5	—	2450.900	1	2	2483.878	15	50
2427.105	3	—	2451.870	15	60	2484.931	4	30
2427.536	9	1	2452.468	—	2	2485.420	2	9
2427.570	—	2*H*	2453.084	20	1	2486.028	—	30*He*

TABLE 2.—*Arc and spark spectra of columbium (Z=41)*—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
2488. 234	3	5	2530. 103	1	2	2562. 402	40	120
2488. 746	—	40*He*	2530. 168	1	3	2563. 913	5	10
2489. 112	2	—	2530. 658	2	1	2564. 070	3	15
2489. 466	—	2	2530. 968	15	80*h*	2564. 265	4	—
2490. 111	1	20*h*	2531. 252	5	30*h*	2564. 526	1	1
2490. 217	2	25*h*	2533. 188	6*c*	30*h*	2564. 735	8	4
2490. 848	—	40*He*	2533. 914	—	20*He*	2564. 846	3	15
2490. 988	—	15*He*	2534. 445	2	10*He*	2565. 098	1	—
2492. 115	—	1	2534. 70	—	2*He*	2565. 410	30	3
2492. 424	1	—	2534. 83	—	2*He*	2565. 504	2	20
2493. 020	—	40*He*	2535. 259	1	—	2565. 675	1	4
2493. 670	—	1	2536. 580	—	1	2566. 075	5	40*He*
2494. 801	3	—	2538. 055	6	1	2567. 281	3	—
2495. 204	1	—	2539. 128	1	—	2567. 42	—	15*He*
2496. 806	—	3	2539. 224	3	10	2567. 510	20	2
2496. 976	2	4	2539. 464	1	—	2568. 409	7	10
2497. 464	2	—	2540. 611	20	80*h*	2568. 677	1	2
2498. 244	3	30	2540. 811	1	3	2569. 030	20	2
2498. 365	1	—	2541. 017	2	—	2569. 187	1	4
2499. 282	2	—	2541. 074	1	2	2569. 796	1	—
2499. 750	—	300*He*	2541. 140	1	—	2570. 782	6	1
2500. 426	4	10	2541. 424	40	50	2571. 054	7	1
2501. 41	—	150*He*	2541. 704	2	—	2571. 324	25	60
2502. 496	10	40	2541. 972	5	—	2571. 74	—	15
2502. 944	4	—	2542. 925	1	—	2572. 090	15	1
2503. 431	1	2	2543. 252	3	—	2572. 80	1	—
2504. 250	—	8*He*	2543. 980	10	1	2573. 022	3	5
2504. 648	30	2	2544. 435	1	1	2573. 136	2	20
2504. 948	1	3*h*	2544. 723	2	—	2573. 914	—	4*He*
2505. 911	2	4	2544. 802	50	200*R*	2574. 074	3*c*	5
2507. 134	6	1	2545. 404	—	2	2574. 843	5	40
2508. 335	—	30*He*	2545. 633	—	200*He*	2575. 570	1	2
2508. 601	2	—	2546. 353	1	2	2575. 968	2	6
2511. 004	30	120*h*	2547. 556	1	2	2576. 592	7	1
2511. 573	3	—	2548. 634	8	30*h*	2578. 086	4	—
2511. 970	—	40*He*	2549. 039	—	1	2578. 203	8	1
2513. 273	2	—	2549. 435	1	2*h*	2578. 734	50	3
2514. 352	6	6	2549. 904	7	—	2580. 284	6	40
2514. 500	1	1	2550. 037	1	2	2581. 194	7	1
2514. 750	1	—	2550. 878	2	—	2581. 465	1	—
2514. 784	3	—	2551. 382	50	120*h*	2581. 971	2	—
2515. 775	4	—	2552. 014	—	4*He*	2583. 103	15	1
2516. 878	1	—	2553. 490	3*c*	15*h*	2583. 219	8	1
2517. 487	2	10*h*	2553. 752	3	—	2583. 982	50*c*	250*R*
2517. 658	—	2*H*	2554. 103	12	1	2584. 450	1	1
2519. 018	2	—	2554. 793	3	8	2586. 087	—	50*He*
2519. 692	3*c*	12*c*	2555. 107	3	—	2586. 911	2	4
2519. 841	2	5	2555. 314	3	8	2587. 409	2	8*h*
2520. 507	10	1	2555. 626	20	60	2587. 952	5*c*	3
2520. 663	—	2*h*	2556. 933	40	120	2588. 36	1	—
2521. 404	40	150*h*	2557. 41	4	—	2588. 966	3	9
2521. 805	2	—	2557. 942	—	100*He*	2589. 264	5	1
2521. 880	2	—	2557. 973	1	—	2590. 940	50	200*R*
2521. 924	3	—	2558. 628	1	3	2592. 035	4	3
2522. 341	3	8	2558. 765	1	—	2592. 190	50	4
2522. 885	—	3*h*	2558. 835	2	—	2592. 911	4	2
2523. 761	2*c*	5*c*	2558. 936	20	2	2593. 530	1	—
2524. 985	10	1	2559. 05	1	—	2593. 764	—	60*He*
2525. 202	1	—	2559. 436	—	2*h*	2594. 337	10	9
2525. 610	2	—	2560. 112	3*c*	6*c*	2594. 685	4	—
2525. 806	20	100*h*	2560. 622	5	20	2594. 736	15	50
2527. 277	4	3	2560. 741	2	3	2594. 964	3*c*	4*c*
2527. 914	5	25	2561. 465	2*c*	2*c*	2596. 498	2	—
2528. 208	1	—	2561. 708	5	6	2596. 96	—	20*He*
2529. 300	1	2	2561. 926	—	1	2597. 138	10	1

TABLE 2.—*Arc and spark spectra of columbium (Z=41)*—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
2597.74	—	20*He*	2631.442	1	3*h*	2664.010	2	3
2598.037	2	6	2632.510	20	60*h*	2665.247	20	80
2598.882	—	100*He*	2633.153	—	80*He*	2666.058	—	2
2599.522	—	3*h*	2633.795	—	1	2666.164	1	3
2600.156	4	10	2633.981	2	—	2666.595	30	50
2600.615	1	2	2634.154	—	20*He*	2667.07	2*c*	4
2601.285	25	100	2634.493	1	—	2667.146	3	10
2601.597	3	—	2634.704	10	2	2667.300	20	30
2601.832	7	1	2634.890	2	—	2667.765	12	35
2602.011	8	1	2635.512	1	—	2667.996	2	4
2602.485	3	4	2635.837	—	3*h*	2668.283	40*r*	3
2603.306	6	1	2636.268	1	—	2668.501	1	5
2603.731	6	10	2637.976	15	10?	2669.512	1	—
2604.225	1	—	2638.15	—	50*He*	2670.152	2	3
2604.753	3*c*	10*c*	2638.591	6	7	2670.524	5	—
2605.013	3	9	2638.877	5*c*	3	2671.255	4	10
2605.064	1	6	2639.39	1	—	2671.447	2*c*	—
2606.204	—	5*He*	2639.420	1	2	2671.656	1	2
2608.114	1	1	2639.883	4	5	2671.933	60	200*rv*
2608.690	1	2	2640.825	2	—	2673.332	2	—
2608.836	6	1	2640.918	20	1	2673.566	40	250*rv*
2608.958	5	10	2641.060	6	30	2674.694	4	—
2609.118	1	—	2641.923	4	—	2674.840	1	3*h*
2609.199	—	1	2642.233	40	120*rv*	2675.104	—	2*h*
2609.444	—	2*h*	2642.566	4	5	2675.945	40	80*rv*
2609.622	1	2	2642.87	1	—	2676.124	2	4
2610.268	20	1	2644.29	1	—	2676.952	3	—
2611.318	2*c*	—	2644.449	2*c*	—	2677.664	6	15
2612.028	1	—	2644.932	1	3	2678.102	3	6
2612.27	—	5*He*	2645.260	—	30*He*	2678.30	1	—
2612.377	15	1	2646.258	60	150*rv*	2678.663	15	8
2613.854	2	8*h*	2646.636	1	—	2679.015	20	1
2613.927	2	7*h*	2647.500	80*R*	5	2679.880	6	—
2614.306	4	7	2648.034	1	3	2680.061	10	50
2614.444	3	—	2648.223	3	—	2681.066	—	1
2614.759	2	10*h*	2649.515	50*r*	3	2682.129	10	1
2616.219	4	15	2649.714	1	4	2682.469	1	8
2616.476	30	2	2650.001	1	—	2682.524	1	—
2616.683	1	2*h*	2650.322	1	—	2682.849	—	2
2617.046	4	—	2650.568	3	—	2683.216	4	6
2617.102	1	3*h*	2651.122	20	80	2683.713	4	—
2617.427	2	10*h*	2651.810	5	10	2686.388	10	120*h*
2618.178	1*c*	—	2652.335	2	—	2686.507	1	—
2618.444	2	3*h*	2652.660	—	2	2687.149	30*r*	3
2618.584	1	—	2652.944	8	1	2689.066	2	4
2620.440	25	80	2653.372	10	1	2689.182	2	—
2620.585	8	1	2653.476	6	1	2689.90	—	2*h*
2622.003	7	1	2654.242	2	—	2690.150	1	2
2622.504	4	—	2654.446	60*R*	4	2690.930	3	4
2622.952	8	20	2655.314	1	2	2691.774	40	60*rv*
2623.170	8	4	2655.695	8	1	2692.002	2	10
2623.321	4	7	2655.865	2	8	2692.652	—	3
2623.507	25	2	2656.076	40	80*rv*	2694.316	2	4
2624.330	2	2	2656.984	10	1	2694.753	2	4
2626.401	2	4	2657.613	40*r*	2	2695.038	30	2
2626.472	3	—	2658.027	—	100*He*	2695.601	—	3
2626.636	2	4*h*	2658.711	1	—	2696.052	8	1
2627.055	1*c*	3*c*	2658.875	4	5	2697.067	100	300*Rv*
2627.435	60	5	2659.049	4	15	2697.66	—	2
2628.408	3	3	2660.036	5	15	2698.05	1	3*h*
2628.493	20	1	2661.124	3	—	2698.540	3	—
2628.679	—	40*He*	2661.852	8	1	2698.866	50	100*rv*
2629.209	2	3	2662.72	1	4*h*+*H*	2700.153	6	15
2630.354	1	1	2663.552	5	10	2700.312	1	3
2630.983	4	20	2663.705	1	2	2700.555	4	5

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
2700.872	4	10	2744.97	2	30c	2779.71	10	2
2702.197	30	60rr	2745.303	5c	20c	2780.235	40c	150c
2702.521	20	40	2745.725	6	40	2780.600	4	1
2704.250	6	20	2746.10	—	30*Hl*	2780.985	—	4
2704.417	4	5	2746.910	30r	3d?	2782.356	20	4
2704.70	—	5	2747.375	—	3	2782.807	—	4
2704.92	—	2	2747.606	—	5	2783.95	1	—
2705.326	1	4	2748.077	—	7	2784.450	—	3
2706.395	10	20	2748.848	30r	3	2785.071	—	6
2707.212	1	3	2749.69	1	4	2785.788	—	2
2707.834	5	20	2749.817	2	5	2786.390	4	1
2709.07	—	2	2750.58	1	15	2788.687	—	3
2709.595	1	3	2752.02	1	6	2789.200	3	1
2711.37	1	5	2752.63	—	3	3789.76	—	8
2712.17	2	—	2752.682	3	—	2790.580	3	10
2713.74	—	2	2753.007	10	—	2790.84	—	4*Hl*
2714.198	5	2	2753.133	6	200c	2791.372	—	5
2715.344	5	50	2753.56	1	5	2791.742	8	80
2715.500	6	—	2753.74	1	3	2792.454	—	1
2715.600	8	—	2754.066	6	1	2793.044	20	80
2715.882	5	40	2754.40	3	—	2793.687	—	3
2716.100	15	1	2754.523	6	40	2793.704	3	—
2716.309	10	15	2755.288	20	2	2793.885	—	7
2716.630	60r	150rr	2755.562	—	5	2793.973	3	—
2717.33	4	10	2755.632	10	—	2795.14	1	15
2717.63	3	8	2755.722	—	3c	2795.868	9	2
2720.024	5	—	2757.256	3	40	2797.215	3	—
2720.259	4	7	2757.50	1	10	2797.693	5c	100c
2720.95	1	6	2758.010	—	1	2798.428	6	1
2721.162	3	6	2758.605	50r	2	2798.903	4	25
2721.632	6	8	2758.78	4	50	2799.180	—	5
2721.987	50r	150rr	2759.160	—	5	2799.354	7	1
2722.310	6	—	2759.968	—	3h	2800.315	10	2
2722.69	2	6	2760.441	2	—	2801.551	—	7c
2723.660	2	40h	2760.91	1	—	2802.066	7	1
2723.986	15	2	2760.990	10	2	2802.73	—	2
2724.95	1	6	2761.737	—	2	2803.54	—	7*H*
2725.33	2	—	2762.32	1	8	2803.810	5	15
2725.68	2	—	2762.49	1	3	2805.83	1	3
2726.080	6	1	2763.025	—	1	2805.98	—	8h
2727.43	2	8	2763.380	15	1	2806.913	—	15h
2728.076	6	1	2763.59	1	15	2808.050	10	1
2729.372	—	5	2764.561	5	10	2808.74	1	6
2729.524	—	2	2764.996	—	2	2809.172	3	8
2729.829	6	1	2765.271	7	9	2809.666	—	4
2730.324	4	60	2765.431	—	2	2810.810	6	100
2732.25	—	2	2765.918	5	—	2811.436	—	2
2733.258	20r	40rr	2765.952	—	6	2811.625	6	—
2733.464	6	8	2766.182	7	2	2811.70	1	15
2733.74	1	15	2767.218	—	5	2814.53	1	—
2734.027	2	—	2767.754	—	2	2815.390	—	20
2734.36	2	15	2768.124	20	100rr	2816.430	2	—
2734.733	—	4	2769.290	—	6	2816.678	3	30
2735.948	—	5	2769.561	3	10	2817.31	1	3
2736.521	—	7c	2769.765	—	1	2818.199	—	20c
2737.083	15	60	2770.907	—	1h	2818.617	—	1
2739.239	—	5	2771.398	4	50	2818.74	3	—
2740.185	8	100	2771.65	2	20	2819.215	15	2
2740.971	—	2c	2773.197	50	5	2819.893	—	15
2741.146	10	—	2774.052	3	1	2820.38	3	—
2741.71	2	—	2774.488	—	5	2820.803	6	12
2742.604	—	4	2774.935	3	1	2821.924	8	1
2742.79	1	—	2775.758	—	6h	2823.34	1	10d?
2743.478	—	8	2778.018	—	3	2823.89	1	10
2744.448	—	4	2779.36	8	2	2824.642	3	1

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
2824.785	4	—	2861.76	2	—	2895.39	—	5
2824.863	—	2	2861.98	—	5*H*	2896.00	—	3*H*
2825.180	10	2	2862.49	1	—	2896.24	5h	—
2825.86	1	8	2864.324	20	4	2896.998	6	2
2826.044	—	3	2865.609	10	60	2897.32	—	1
2826.47	12	6	2866.672	8	2	2897.345	6	—
2826.97	—	4h	2866.86	—	2	2897.605	4	—
2827.071	25	?	2867.28	—	10h	2897.803	30	200*R*
2827.116	?	30	2868.524	30	300*R*	2899.230	40c	200r
2827.79	—	2	2868.96	2	—	2900.67	—	40*H*
2827.93	—	3	2869.84	—	3	2900.782	1	—
2828.950	3	1	2870.37	—	10*Hl*	2901.692	1	—
2829.367	3	1	2870.654	5	—	2902.329	—	2
2829.750	6	15	2871.06	—	2h	2902.60	—	5*H*
2830.56	1	20	2871.238	3	—	2903.16	—	2*H*
2830.85	—	3	2871.65	—	2h	2903.650	10	3
2832.78	—	10h	2871.91	—	1	2904.13	—	3
2833.312	—	8	2872.51	—	1	2904.87	—	6
2833.51	3	—	2872.81	1	7	2905.56	—	4*H*
2833.648	4	—	2872.93	1h	—	2906.422	3	—
2835.106	6	50	2873.68	2h	—	2906.80	—	6*H*
2836.079	—	4	2874.564	15	2	2907.206	—	1
2836.245	30	4	2874.98	—	1	2907.53	—	4*H*
2836.45	—	3h	2875.386	50c	300c*R*	2908.236	40	200r
2839.13	—	5*Hl*	2876.951	30	150	2908.88	5	?
2839.62	—	7h	2877.026	50	200c*R*	2908.93	?	120r
2839.79	1	6	2877.62	—	10	2908.97	2	?
2840.57	—	1	2877.85	3	10	2909.25	1	—
2840.929	10	2	2878.16	3	—	2910.580	50	400*R*
2841.141	40c	80c	2878.739	8	9	2910.69	2	—
2842.018	6	2	2878.818	3	—	2911.08	2	—
2842.642	30	100r	2879.21	—	3h	2911.740	20	200*R*
2843.41	—	3h	2879.359	4	15	2912.75	1	—
2843.640	3	20	2879.492	8	—	2912.91	—	2
2844.428	3	40	2879.97	1	—	2913.135	2	—
2845.32	—	10*Hl*	2880.712	10	100	2913.72	—	1h
2845.52	2	—	2881.17	1h	1h	2914.41	—	5h
2845.798	5	20	2881.31	1h	1h	2915.059	2	—
2846.280	20	60	2881.84	—	3h	2915.18	1	—
2847.23	1	15	2882.471	1	10	2915.412	2	10
2847.89	1	—	2883.168	60c	300c*R*	2916.09	—	8c
2848.02	1	6	2883.60	—	4h	2916.40	—	3
2848.296	5	20	2883.626	1	—	2916.500	5	—
2849.04	—	10*Hl*	2883.89	1	—	2917.050	8*d*	100
2849.557	5c	100c	2884.968	12	3	2918.56	—	10
2850.385	—	4	2885.451	2	—	2918.92	1	3
2851.295	—	5	2886.24	—	1	2919.32	—	3
2851.446	20	2	2886.34	1	7	2919.516	1	—
2851.82	—	1	2886.61	—	3	2922.30	—	1h
2851.978	15	2	2887.088	2	8	2922.45	—	6
2853.264	3	—	2887.294	6	1	2922.74	—	1h
2853.52	1	3	2887.52	1	—	2923.025	8	1
2854.168	12	3d?	2887.70	5	10	2924.824	10	2
2855.082	—	3	2888.824	30c	150r	2925.15	—	2
2855.54	1	8	2889.898	10	1	2925.360	8	1
2855.82	—	2*H*	2890.174	6	—	2925.77	—	2
2857.294	10	—	2890.350	2	10	2925.89	1h	—
2857.363	—	7	2890.56	1	5	2925.93	—	4
2858.42	—	5*Hl*	2891.01	—	3*Hl*	2926.08	—	1
2858.974	10d?	—	2891.41	—	10*Hl*	2926.30	—	2h
2859.038	—	20	2893.04	—	8*Hl*	2927.804	100c	600c*R*
2859.46	—	2	2893.47	3h	—	2929.13	2h	—
2859.962	15	2	2894.43	3c	20c	2929.662	4	1
2861.091	20	100	2894.77	1	—	2930.267	—	60
2861.66	—	3	2894.90	3	—	2930.648	—	7

TABLE 2.—*Arc and spark spectra of columbium (Z=41)*—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
2930.853	—	3	2974.094	25	400*rv*	3007.488	—	4
2931.33	4*Bl*	—	2974.54	5	—	3007.86	2*h*	—
2931.458	10	70	2974.72	—	10	3008.39	—	20*c*
2932.13	—	30	2975.92	—	2	3008.97	—	7
2932.658	1*h*	25	2976.150	1	1	3009.86	—	1*h*
2932.93	1*h*	—	2977.67	4*c*	150*c*	3010.38	1	20
2933.17	—	2	2978.09	—	2*h*	3010.685	1	25
2933.43	—	2	2978.943	4	80	3011.61	—	10*Hl*
2934.980	5	1	2979.34	—	3	3012.546	5	1
2935.282	4	20	2979.50	—	1	3013.27	3*h*	—
2935.75	—	1*h*	2979.875	4	80	3013.62	—	3
2936.36	—	1*h*	2980.717	7	150	3014.438	5	15
2936.50	—	3	2981.28	1	—	3015.02	—	30
2936.67	—	20	2981.636	15	2	3015.24	8	1
2937.327	5	25	2982.100	20*d*	100	3015.82	1	20
2937.707	—	100	2982.90	—	3	3016.19	—	2
2938.067	15	3	2983.13	5	—	3016.258	1	—
2939.67	—	1*h*	2983.57	—	3*H*	3018.31	—	7
2940.88	—	4	2984.077	4	1	3018.853	3*d*	100
2941.536	60*c*	500*cR*	2984.60	1*h*	—	3019.07	1	6
2942.10	1	—	2985.04	3*h*	50	3019.20	—	3
2943.42	—	1*h*	2986.02	1	—	3019.34	2*h*	—
2944.63	5*Bl*?	—	2986.40	—	5*h*	3019.57	—	8
2945.74	6	—	2986.84	3*h*	—	3019.780	3*h*	3
2945.890	12*c*	100*c*	2986.90	—	3	3020.668	20	2
2946.110	10	60	2987.16	—	1	3020.866	—	2
2946.890	10	80	2987.286	15	1	3021.08	—	3
2948.060	2	—	2987.55	—	9	3021.885	—	8
2949.15	1*d*	—	2988.13	1*h*	—	3022.48	—	5
2949.506	—	4	2988.692	6	2	3022.738	8	200
2950.70	2	—	2988.789	6	1	3023.38	2	—
2950.876	80*c*	800*cR*	2989.63	1	—	3024.258	3	10
2952.53	—	1*h*	2989.944	—	40*h*	3024.735	20*c*	250
2952.75	—	1	2990.28	30*c*	200*c*	3025.372	2	40
2952.95	—	1	2991.35	1*h*	—	3026.53	2*h*	—
2953.384	—	2	2991.43	—	6	3026.80	—	2*h*
2954.03	3	5	2991.956	6*c*	80	3027.16	1	—
2954.538	2	20	2992.084	5	—	3027.89	7	2
2954.72	—	4*h*	2993.806	2	20	3028.436	80*c*	300*c*
2955.444	5	2	2993.97	—	20*c*	3028.69	7	—
2956.89	1	20	2994.725	80*c*	300*c*	3028.76	—	10
2958.66	—	1	2995.49	—	4	3029.17	4	1
2958.86	—	1	2996.49	6*h*	2*h*	3029.23	3	—
2959.90	—	2	2996.79	1	7	3029.76	4	60
2959.973	3	1	2997.14	—	1	3029.86	—	20
2960.231	—	3	2997.48	1	8	3030.79	—	2*h*
2961.64	1*h*	15	2997.947	—	1	3032.767	40+8*n*	400*rv*
2962.12	2*Bl*	—	2998.220	5	2	3033.396	5	—
2962.288	1	—	2998.312	1	—	3033.47	—	4
2963.205	—	1	2998.56	—	1	3034.95	—	200*cR*
2963.682	5	2	2998.87	—	4*h*	3035.03	3	—
2964.958	—	3	3000.11	7*h*	—	3038.18	—	10*Hl*
2965.11	2*Bl*	—	3000.72	4	—	3039.19	7	2
2965.48	10	3	3001.125	3	50	3039.398	6	10
2965.63	—	6	3001.85	—	150	3039.68	20	—
2965.871	—	8*c*	3002.204	5*d*	40	3039.818	20*c*	150*c*
2967.93	—	3*h*	3003.16	—	2*h*	3040.25	3	—
2968.29	1*d*	10	3003.208	2	—	3040.54	—	4
2969.594	1	—	3003.75	—	3*h*	3040.67	1	—
2970.40	—	10	3004.49	1	—	3041.358	5	2
2970.47	—	10	3004.65	—	10	3041.660	5	1
2972.568	50*c*	200*c*	3005.141	9	2	3041.89	5	—
2973.32	—	6	3005.764	3	60	3041.98	—	10*c*
2972.47	3	—	3006.964	3	1	3042.790	2	15
2973.83	1	—	3007.284	1	—	3043.272	2	10

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
3045.546	5	1	3078.92	—	1h	3113.061	4	—
3046.67	2h	6h	3079.11	—	1h	3113.17	1	30
3048.093	20	—	3079.37	—	1h	3114.38	2h	—
3048.21	2c	80c	3079.71	—	1h	3114.51	1	—
3048.63	1	5	3080.345	15c	100	3114.78	—	2
3049.02	—	1h	3081.09	—	8	3115.16	—	15
3049.528	2c	40c	3081.77	2	40	3115.533	2	20
3051.34	1	15	3082.38	—	1h	3116.366	15	3
3051.666	6	1	3082.859	10	2	3116.57	1	10c
3051.77	1	—	3083.32	—	30c	3117.33	—	1h
3051.990	8	2	3083.607	1	—	3117.65	1	—
3052.73	5	1	3083.828	2	—	3118.948	1	—
3052.988	6	2	3084.369	2	50	3119.402	6	—
3053.086	10	3	3084.760	—	2	3119.48	—	6c
3053.631	3	90	3084.94	4h	—	3120.276	3	1
3054.14	3	—	3085.67	1h	—	3120.878	5	—
3054.47	1	—	3085.81	—	1	3121.35	3h	—
3055.520	6	200	3086.09	—	20h	3121.66	2h	—
3056.608	9	2	3086.475	2	1	3121.964	5	2
3057.03	—	12	3087.625	4	2	3122.13	1h	—
3057.57	—	1h	3087.75	1h	—	3122.646	15	3
3058.62	—	3	3087.860	6	90	3124.62	—	2*H*
3059.294	1	20	3088.05	9	2	3124.72	1h	—
3060.39	5	—	3088.24	1	—	3125.12	3	—
3060.844	—	4	3089.110	—	3	3125.197	2	—
3061.100	8	2	3090.13	2	—	3125.46	—	2*H*
3061.232	10	1	3092.89	1	6	3125.892	1	10
3061.408	—	5	3093.65	1	—	3127.526	30	500
3061.78	2	—	3094.172	200c	2,000c*R*	3127.690	2	—
3061.95	1	10	3094.37	5	—	3128.372	5	20
3063.126	3*d*	40	3095.22	2	—	3128.57	—	1h
3063.782	9	120	3096.490	10	2	3128.92	2h	10
3064.530	40	250*r*	3097.115	3c	60c	3129.14	2	—
3065.26	20c	100c	3098.300	3h	—	3129.554	4	—
3066.09	5	60	3098.47	2	10	3129.65	3c	60
3066.41	3	—	3098.780	2	—	3130.780	150c	1,500c*R*
3066.49	—	4	3098.98	2	—	3131.61	2h	—
3066.59	3*d*?	—	3099.180	15	100	3132.015	1	10
3067.523	1	20	3100.163	3	—	3132.140	1	4
3068.06	1	20	3100.25	—	50	3132.589	2	—
3068.93	—	5	3100.79	—	20	3132.767	3	60
3069.023	10	5	3100.97	5	—	3132.881	1	—
3069.51	—	5	3101.064	2	—	3133.088	15	3
3069.68	15	100	3101.69	1h	—	3133.89	1	—
3070.893	7	80	3101.918	2	20	3134.342	4c	40
3071.18	5	40	3103.26	1	4	3134.620	2	—
3071.34	1	—	3103.39	1	—	3134.765	1	—
3071.55	10c	90c	3104.27	—	8	3134.835	1	—
3071.77	2	—	3104.62	—	2	3135.409	3	25
3072.18	—	10	3104.86	2h	—	3135.920	4	30
3072.206	7	—	3105.79	1	—	3136.49	1	—
3072.397	10	—	3106.520	1	10	3136.972	15	3
3072.502	2	60	3106.980	4	30	3137.27	—	3
3073.232	10*d*	50	3108.07	3	—	3137.98	—	2h
3074.27	1	5	3108.84	—	1h	3138.888	1	—
3074.447	3	—	3109.30	—	1h	3140.506	8	100
3075.250	1	10	3109.735	5	1	3140.97	—	4
3075.816	3	—	3110.800	1	20	3142.26	—	100c
3076.23	—	1h	3111.446	20	3	3142.384	2	—
3076.49	2	—	3111.558	2	—	3142.644	2	—
3076.864	30*d*	200	3111.63	—	5	3142.926	1h	—
3077.44	1	10	3111.79	1	—	3143.17	—	3
3077.70	1	—	3112.08	2h	—	3143.41	—	4
3077.800	3	—	3112.36	2h	—	3143.44	1	—
3078.28	—	1h	3112.630	3*d*?	—	3143.77	—	1h

TABLE 2.—*Arc and spark spectra of columbium (Z=41)*—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
3144.333	4	60	3175.86	10	150	3203.357	10	150
3144.45	1h	—	3176.14	—	4	3204.340	4	—
3145.405	50	500rr	3177.41	—	2	3204.66	2c	—
3145.920	5	—	3177.766	1	6	3204.973	5c	100c
3146.863	2	—	3178.17	1	—	3205.975	3	—
3146.92	3	30	3178.23	—	1	3206.11	1	—
3147.57	—	1h	3178.632	2	—	3206.350	50	300rr
3147.625	2	—	3179.242	1	8	3206.812	5	—
3148.30	—	1	3180.290	50	400	3207.341	5	20
3148.710	6	1	3180.79	2	—	3207.56	—	2
3150.06	—	1	3181.11	1h	—	3207.64	1h	—
3150.409	5	50	3181.403	8	40	3208.10	1h	8
3150.95	1	—	3182.053	5	1	3208.409	1	3
3151.870	30	4	3182.399	4c	1h	3208.585	2c	40c
3152.160	5	200	3182.94	—	3H	3208.86	3	—
3152.785	4	70	3183.135	1	—	3210.20	—	4
3153.38	—	4h	3183.48	1c	—	3210.29	15	4
3153.851	1	10	3184.229	6	150	3210.787	2	—
3153.98	10	2	3184.77	1	—	3211.40	—	3h
3154.321	2	—	3184.94	—	2	3211.63	—	2h
3154.820	4c	150c	3185.23	—	2	3211.814	2	20
3155.599	3	30	3185.55	2	—	3212.14	1	10
3155.73	1	—	3186.24	—	1h	3213.24	1	—
3155.888	2	—	3186.550	15	3	3213.45	1h	2d?
3156.00	—	3	3187.15	—	1h	3213.884	5	—
3157.34	—	2	3187.497	40	4	3213.91	—	3
3157.73	2	—	3188.36	1	4	3214.507	2	—
3158.104	2	10	3188.85	—	4	3215.000	—	5h
3158.962	2	—	3189.288	10c	180c	3215.229	10	1
3159.21	2h	—	3189.560	4	—	3215.595	60c	300cr
3159.332	6	1	3190.44	—	6	3215.959	1	—
3159.855	2	15	3190.490	3	—	3216.193	2	6
3160.59	—	2h	3191.096	100c	200c	3216.43	1	—
3160.60	3	—	3191.427	15	250	3216.47	—	2
3161.194	8	—	3192.16	—	3	3217.00	2c	60c
3161.244	—	4c	3192.39	—	2	3217.288	30	3
3161.49	1	—	3192.73	2	—	3217.865	20	2
3161.56	—	4	3193.003	4c	—	3217.797	6	1
3163.149	3	10	3193.47	—	3	3218.98	1h	3h
3163.403	100R	1,000R	3194.27	2c	30c	3219.55	—	2
3164.488	2	—	3194.367	3	—	3219.681	6	—
3164.76	—	1h	3194.64	1	—	3219.91	—	1h
3165.24	—	1	3194.75	1	—	3220.14	2h	—
3166.230	1	—	3194.983	100r	700R	3220.48	1h	4h
3166.49	1h	—	3195.22	2	—	3220.927	15	3
3166.59	2h	—	3195.96	—	2	3221.126	15	3
3167.32	—	3h	3196.17	—	3	3221.436	2	—
3167.96	—	1	3196.18	5	—	3221.53	1	—
3168.141	2	—	3196.71	1h	—	3221.655	—	3c
3168.509	8	1	3197.28	—	20h	3222.065	6	30
3170.163	4	1	3197.94	1h	—	3222.754	7	1
3171.168	6	2	3198.182	3	—	3222.958	6	1
3171.425	10c	1	3198.227	2	20	3223.004	3	—
3171.80	—	50h	3199.88	—	4h	3223.332	10	100
3172.25	—	5h	3200.102	3c	—	3223.448	1	—
3172.304	4	—	3200.24	—	3h	3223.751	3c	—
3172.511	12	2	3200.537	15	2	3223.903	2c	—
3173.205	10	150	3200.69	—	1	3224.434	8	1
3173.677	4	—	3200.78	—	1	3225.009	2	—
3174.44	—	6h	3201.21	—	1h	3225.194	9	—
3174.73	—	1	3201.498	4	—	3225.478	150c	500cR
3175.40	—	1	3201.66	—	3	3227.209	2	—
3175.68	3	—	3202.416	1	—	3227.49	2h	—
3175.76	3	50	3202.73	1	—	3227.69	—	6
			3203.148	—	10h	3227.711	4	—

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
3228.47	—	6	3253.339	4*d*	—	3279.248	7*c*	20*c*
3228.953	1	6	3253.45	1*h*	—	3279.43	1	4
3229.19	4	1	3254.070	60	200*r*	3279.826	8	—
3229.455	1	—	3254.455	2	—	3279.979	3	80*h*
3229.567	20	100	3254.71	2	—	3280.96	—	1
3230.243	3	40	3254.888	3	25	3281.28	—	2*h*
3230.53	1	—	3255.27	1	5*h*	3281.62	—	2*h*
3230.794	2	—	3255.590	2	—	3282.608	1	—
3231.336	1	—	3255.80	—	1*h*	3282.77	—	1
3232.661	2*h*	—	3256.03	1	—	3282.990	5	—
3232.79	—	5*h*	3256.15	—	5*H*	3283.463	25	400
3232.891	2	—	3256.75	—	2	3284.04	1	—
3232.984	3	—	3257.004	3*c*	1	3284.81	1	—
3233.92	—	2*h*	3257.17	1	—	3284.890	2*c*	—
3234.182	—	2	3257.65	1*h*	—	3285.381	3	—
3234.26	1	1	3258.39	—	4*H*	3285.488	1	—
3234.65	1	—	3258.85	1	—	3285.668	60	?
3235.066	1	—	3259.140	6	1	3285.70	?	30*c*
3235.182	2	—	3259.523	—	1	3286.340	1	40
3235.78	—	2*h*	3260.139	20	2	3286.81	—	5
3236.078	2	—	3260.564	30*c*	350*c*	3287.592	50	4
3236.403	80	300*r*	3261.036	2	—	3287.72	1*h*	—
3236.704	2	—	3261.702	3	60	3287.75	—	3
3236.810	1	—	3261.88	—	3	3287.923	40	5
3237.187	8	—	3262.56	—	6	3288.19	3*h*	—
3237.690	4	60	3263.365	10	300	3289.460	8	1
3238.020	10*c*	80*c*	3263.793	3	—	3289.551	2	10
3238.394	3	—	3264.261	2	—	3289.82	—	1
3238.975	2	—	3264.597	40	5	3290.007	15	2
3239.23	—	2*h*	3265.313	5	1	3290.30	1*h*	—
3240.582	3	—	3265.53	—	1*h*	3290.55	—	3
3241.111	1	—	3266.008	6*c*	—	3291.055	10*c*	30
3241.29	—	3	3266.11	—	80*c*	3291.921	10	—
3241.818	3	40	3266.413	9	—	3292.020	15	200
3242.423	1	8	3267.052	15	4	3292.365	2*c*	10*c*
3242.532	5	40	3267.684	3	30	3292.806	2	—
3242.67	1	—	3268.946	2	—	3294.250	1	—
3242.928	3	—	3269.125	3*c*	20	3294.367	4	150
3243.322	4	—	3269.493	3*c*	—	3295.506	1	20
3243.725	1	—	3269.87	—	2*H*	3296.025	80	10
3243.83	—	6	3270.465	25	4	3296.478	10	1
3244.20	1*h*	—	3270.761	20	4	3297.055	7	20
3244.515	2	30	3270.93	—	2*h*	3297.286	8*d*	—
3244.684	2	—	3271.55	—	5*H*	3297.673	5	15
3244.784	2	—	3271.962	10	3	3298.410	12	2
3245.07	—	5	3272.074	25	5	3298.977	4	1
3245.59	—	2	3272.224	5	100	3299.29	—	1*h*
3246.69	—	6	3272.350	1	10	3299.57	—	50
3246.76	—	3	3273.139	3	—	3299.608	30	—
3246.782	15	—	3273.511	5	20	3300.33	1	6*h*
3247.478	12*c*	150*c*	3273.758	1	—	3300.81	—	1*h*
3247.575	1Cu?	—	3273.888	3	15	3301.498	2	40
3247.645	3	—	3274.355	2	—	3301.96	—	3
3248.18	1*h*	—	3274.455	—	1	3302.183	15*c*	2
3248.941	10	80	3274.796	3	30	3302.48	3	—
3249.517	50	5	3275.13	2	—	3302.619	1	10
3250.27	1*h*	40	3275.960	5	1	3302.80	1*h*	—
3250.448	1	—	3276.304	2	—	3303.07	3*c*	—
3250.897	1	—	3276.43	—	6	3303.323	3	50
3251.260	3	50	3276.567	4	—	3304.71	1	40
3251.490	9	—	3277.30	—	3	3304.836	20	5
3251.630	30	3	3277.676	50	5	3305.608	3	70
3252.430	1	10	3277.77	—	4	3306.29	1	—
3252.771	7*c*	—	3278.307	1	—	3306.778	3	1
3253.16	—	1	3278.599	4	—	3308.050	40	4

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
3308.710	2	—	3333.970	10	2	3357.156	—	2
3308.78	1	—	3334.529	—	8c	3357.899	4d	1
3309.26	—	5	3334.82	2	8	3358.422	250r	40
3309.617	2	1	3335.244	2c	10c	3358.77	4	1
3309.805	6	2	3335.420	20c	3c	3359.874	7	1
3310.097	5	2	3335.669	—	5c	3360.904	6	100
3310.37	2	—	3336.04	1	—	3361.35	2	—
3310.469	25	3	3336.321	15	2	3361.86	2d	—
3310.67	—	20h	3337.20	—	2h	3362.17	—	20h
3311.341	15	4	3337.87	4	—	3362.866	10	2
3311.75	2c	—	3338.38	—	3	3363.34	—	2h
3311.95	1c	—	3339.158	12c	2c	3363.750	15d	2
3312.607	120	15	3339.268	8	1	3365.594	15	100
3313.08	—	3h	3339.40	—	1h	3365.883	6	?
3313.41	—	4	3339.783	6	1	3365.94	2	100
3313.64	—	2	3340.18	—	4h	3366.956	50	10
3314.10	1	—	3340.45	1	60d	3367.085	8	2
3314.587	2	—	3341.612	10	150	3367.382	25	4
3315.226	40	5	3341.982	200r	20	3367.867	—	2h
3315.979	1	—	3342.360	4	1	3368.426	10d	2
3316.61	1	15	3342.48	2	—	3369.081	20c	?
3317.04	1	1h	3342.912	4	—	3369.155	5	100
3317.363	2h	2h	3343.28	—	5	3369.719	4	—
3318.29	1	5	3343.712	150r	15	3369.840	20d	2
3318.461	2	—	3343.90	3	—	3370.154	—	50
3318.982	50	5	3343.967	8	80	3370.609	4	30
3319.22	—	10c	3344.25	1	8h	3371.331	40	6
3319.265	40	?	3344.41	1	—	3372.101	10	2
3319.590	15	100	3344.50	1	—	3372.164	6	—
3320.124	—	1	3345.16	—	2h	3372.565	8	120
3320.56	—	2	3345.178	4	—	3373.71	1	—
3320.808	5	80	3345.40	2c	—	3374.029	5	—
3321.53	4	—	3345.949	5	—	3374.087	—	20h
3321.81	—	1h	3346.09	1	—	3374.252	6	50
3321.846	2c	—	3346.286	—	20c	3374.928	60	10
3322.00	2	—	3346.760	10	30	3376.341	12	3
3322.245	6	1	3346.935	25	5	3376.59	1	—
3322.68	4c	—	3347.558	6	1	3376.732	15	3
3322.816	8	2	3348.082	4	—	3377.09	—	2h
3323.22	—	3h	3348.28	2h	20	3377.375	—	9c
3323.900	3	30	3348.787	1	15	3377.743	6	1
3324.555	4	30	3349.068	200r	10	3378.162	1	1h
3324.661	2	50	3349.351	3	100	3379.300	4	60
3325.21	—	4h	3349.524	40c	2c	3380.055	20	3
3325.436	—	20h	3350.048	4	—	3380.420	40	4
3325.744	6	—	3350.41	—	3h	3380.490	7	—
3325.946	1	—	3350.689	7c	1	3380.862	20	?
3326.077	1	—	3351.33	2h	—	3380.934	3	150
3326.54	—	7	3351.511	1	—	3382.44	2c	40h
3326.621	50	6	3351.819	3c	—	3382.91	2	2
3326.745	4	—	3351.87	—	3h	3383.302	—	10c
3327.246	—	3h	3352.282	12	2	3383.802	15	3
3327.415	1h	—	3352.502	15	2	3384.50	1h	—
3327.923	10	2	3352.828	—	5h	3384.662	20	4
3328.163	6	1	3352.868	10c	—	3385.192	4	1
3328.398	6	1h	3353.352	7d	1	3385.665	12	2
3328.844	1	—	3353.509	15	10	3385.815	10	2
3329.16	—	20h	3353.675	6d	—	3386.243	20	250
3329.364	40	3	3354.743	80	15	3386.995	20	3
3329.622	10	2	3355.423	12	2	3387.579	10	3
3331.67	1h	—	3355.67	—	1h	3387.754	15	3
3331.895	10	2	3355.92	—	3h	3387.928	—	2h
3332.164	25	4	3356.465	8c	—	3388.537	—	1h
3332.704	15	3	3356.76	1	—	3388.939	4	30
3333.516	1	—	3357.043	25	4	3389.046	1	—

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
3389.73	1	—	3420.11	7*d*	1	3452.373	20c	?
3390.08	1c	—	3420.287	4	—	3452.652	15c	2c
3390.413	7c	1	3420.633	10	80	3453.08	3c	—
3390.623	25c	4c	3421.161	5c	20c	3453.425	2	—
3391.332	10	2	3421.318	—	3	3453.96	—	5c
3391.429	7	1	3422.06	—	1*h*	3454.708	4	60
3391.594	2	9	3422.119	1	—	3454.910	4	80
3391.732	4	—	3422.35	1	—	3456.543	12	3
3392.345	100	10	3422.77	2	5	3456.993	5*h*	?
3392.475	—	4*h*	3422.85	1	10	3457.04	?	4*h*
3393.679	2	—	3423.23	2*h*	—	3457.205	2	—
3393.810	2	10	3423.643	—	5c	3457.801	20	3
3394.090	12	1	3423.765	30	4	3458.728	?	10
3394.217	6	1	3424.30	—	1*h*	3458.740	7	?
3394.978	8	60	3425.432	30*d*	300c	3458.87	5	—
3395.455	4	—	3425.855	30c	2	3458.951	12	2
3395.72	3	15	3426.562	25*d*	250c	3459.56	—	15
3395.928	40	3	3426.730	4c	—	3459.702	25	5
3396.365	6	50*h*	3427.454	50	7	3460.66	5	—
3397.319	—	10*h*	3427.74	—	1*h*	3461.54	—	4c
3397.43	1	—	3428.369	7	1	3461.61	5	—
3397.516	—	5*h*	3428.795	15c	3c	3462.647	15	3
3397.836	2	—	3429.059	20	5	3463.033	10	3
3398.254	15	6	3430.428	—	2*h*	3463.685	8	2
3399.399	25	4	3430.912	—	2*h*	3463.813	25c	10c
3399.714	15	30	3431.064	8*d*	—	3465.610	3	—
3399.967	10	1	3431.18	—	4*h*	3465.860	30	3
3401.231	8	10	3431.955	10	1	3466.231	2	—
3402.02	2	20	3432.420	15c	1c	3467.474	15	3
3402.40	1	—	3432.708	10	400	3468.127	—	15c
3402.81	—	2*h*	3433.099	12	1	3468.17	1	—
3403.013	15c	2c	3433.18	6	—	3468.374	1	3
3403.49	—	3*h*	3433.747	—	5*h*	3468.549	8	2
3403.755	10	2	3433.952	—	3	3468.942	3	—
3404.512	4	—	3434.118	4	—	3469.135	7	1
3404.989	1	—	3434.588	—	2*h*	3469.244	3	—
3405.418	60	10	3435.02	—	2*h*	3469.442	15	3
3406.140	40	6	3435.04	3*h*	—	3470.27	5*d*	50
3406.616	10	2	3435.583	—	2*h*	3471.036	5	—
3406.947	—	10*h*	3435.899	—	2*h*	3471.198	10	2
3407.32	1	10	3436.834	4	20	3471.28	2c	—
3407.980	10	4	3436.964	15	60	3471.526	9	1
3408.380	50	5	3438.41	1	80	3472.776	5	1
3408.53	—	3*h*	3439.342	8	2	3473.020	30c	5c
3408.678	20	100	3439.702	4	—	3473.125	7	2
3409.191	20	100	3439.925	10	60	3473.362	5c	—
3409.915	15	2	3440.589	30	200	3474.004	4	20
3410.66	1	1*h*	3441.64	5c	10c	3474.68	5c	25c
3410.96	—	1*h*	3442.655	12	2	3474.99	1	—
3411.50	—	1*h*	3442.800	10	1	3475.590	15	3
3412.480	1*h*	10*h*	3443.737	1	20	3475.990	10c	2
3412.934	25	150	3444.281	4	60	3476.28	—	6
3413.209	2	20	3445.67	40c	8c	3476.655	1	—
3413.51	10*d*	1	3446.382	1	—	3477.26	1	—
3414.070	15	3	3446.747	3	—	3477.92	1	—
3415.22	1	2*h*	3446.928	1	5	3478.010	8	1
3415.603	4	—	3447.843	1	—	3478.335	4	1
3415.984	30c	5c	3448.221	4	40	3478.690	40	4
3416.32	—	1*h*	3448.674	2	20	3478.79	7	100
3417.17	—	5*h*	3448.76	1	—	3479.567	20	150
3417.272	5*d*	—	3450.766	6	60	3480.213	4	80
3417.80	—	2	3451.12	3c	—	3481.054	15	3
3417.867	15	5	3451.640	1	20	3481.265	9	2
3418.31	1*h*	2*h*	3452.19	—	3*h*	3481.82	2	—
3419.148	1	—	3452.350	?	40	3482.19	1	—

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
3482.52	1	5h	3514.911	3c	—	3544.346	1	15h
3482.953	2	100	3515.421	20c	200c	3544.656	50	8
3483.23	1	—	3516.198	10	2	3545.381	6c	1c
3483.754	3	—	3516.342	3	—	3546.031	12	2
3484.054	15	80	3516.863	15	3	3546.160	5	1
3484.625	5	10	3517.111	10	3	3546.489	8	1
3485.102	8	1	3517.670	6	150	3546.910	2	—
3485.935	12	3	3517.77	12	—	3547.016	1	—
3486.724	7c	2	3517.84	5	—	3547.426	3	—
3487.52	2	—	3518.180	8	1	3548.08	—	4h
3487.814	1	—	3519.337	6	2	3548.130	15	2
3487.968	1	—	3519.66	—	5h	3549.263	12	2
3488.50	1	—	3520.055	40	5	3549.96	1	—
3488.742	2	—	3520.717	12	2	3550.237	10	1
3488.81	3	80	3521.14	1	20h	3550.448	50	7
3489.093	10	90	3521.599	—	5h	3550.624	6	1
3490.12	1	—	3522.368	—	10h	3551.102	8	4
3490.418	—	10	3522.630	2	—	3551.37	1	—
3491.024	50d	7d	3522.787	6	2	3552.000	5	1
3491.477	15	3	3523.156	12	2	3552.227	6	—
3491.896	1	20	3524.93	8	2	3552.815	1	—
3492.56	3	—	3525.219	30c	5c	3553.613	10c	—
3493.476	5	1	3525.88	8	—	3554.14	1	6h
3494.57	3	1	3525.986	—	50h	3554.524	60	6
3495.18	1	—	3526.209	2	—	3554.666	80	8
3495.473	3d	1	3527.024	—	8c	3555.63	1	—
3495.71	1	—	3527.108	10	1	3556.022	10	2
3496.027	20c	30c	3527.280	6c	—	3557.023	2	—
3496.284	2d	—	3527.959	10	2	3557.684	1	—
3496.879	1	—	3528.00	—	5	3558.015	9	2
3497.646	5	2	3528.315	10c	—	3559.128	12	2
3497.815	30	5	3528.474	4	30	3559.470	1	—
3498.358	3c	—	3528.890	2	20	3559.592	4	60
3498.441	5	1	3529.394	8c	1	3559.893	—	6h
3498.631	60c	10c	3530.093	10	2	3559.92	1	—
3498.783	7c	—	3530.824	7	2	3560.357	7	—
3499.93	—	30c	3531.305	1	—	3560.47	1	5
3499.957	8c	—	3532.521	5c	—	3561.142	12	2
3500.109	8	1	3533.667	40	4	3561.697	6	1
3500.74	—	10h	3534.05	?	10h	3561.88	—	4
3500.96	1	—	3534.114	20c	?	3562.649	6c	1
3501.32	1	15	2534.215	3	50	3562.846	3	1
3503.206	20	3	3534.428	7	—	3563.232	6	1
3504.59	1	—	3534.85	1h	—	3563.501	100	7
3505.629	2	—	3535.304	400c	20c	3563.624	80	5
3505.812	12	2	3535.845	1	—	3564.028	6c	—
3505.992	—	5c	3536.212	4c	1	3564.075	—	15h
3506.025	7	—	3537.106	1	—	3565.052	10c	—
3506.991	10	2	3537.157	1	—	3565.23	—	1
3507.960	80	7	3537.475	150	6	3565.68	—	3h
3508.21	1h	—	3537.625	8	40	3565.855	6	—
3508.529	8c	1	3538.076	2	—	3566.10	—	40h
3509.872	1	—	3538.58	2	—	3566.33	2	—
3510.262	20c	400	3538.62	—	2h	3567.009	5c	—
3510.41	1d	—	3539.11	—	6h	3568.001	4	40h
3511.13	10c	1	3539.650	15d	3	3568.50	?	30
3511.189	20c	2	3540.961	30	200	3568.515	10c	?
3511.614	1	—	3541.247	6c	50	3568.727	20	3
3512.309	5	1	3541.898	20c	3c	3569.464	40	6
3512.749	6	1	3542.560	10	2	3569.692	5	1
3513.24	1	—	3542.983	15	4	3569.854	7c	1
3513.545	2	—	3543.55	1	—	3571.124	3	—
3513.673	3	—	3543.745	5	1	3571.485	6c	—
3513.721	2	—	3543.936	12	2	3572.10	1	—
3514.02	—	20c	3544.031	50	6	3573.096	5	1

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
3573.42	2c	—	3607.01	3	15	3637.830	35c	4c
3574.202	1	10	3607.33	7	3c	3637.86	—	15h
3574.312	3	—	3608.013	10d	2	3638.673	2c	—
3575.139	20c	3	3608.316	9	2	3638.792	20c	2
3575.55	1	—	3609.24	1	—	3639.058	4	30
3575.850	200	20	3609.362	1	6	3639.335	40c	6c
3577.238	8c	2	3610.002	8c	1	3640.638	30	4
3577.721	40	6	3610.765	7	2	3641.293	1	15
3578.23	4	1	3611.285	7c	1	3641.382	2	20
3578.317	3	—	3611.39	—	3	3641.514	3	—
3578.38	—	2	3612.165	1	—	3641.571	3	—
3578.586	4c	1	3612.657	9	2	3642.587	2	—
3579.186	3	—	3613.013	9	2	3643.343	15	3
3580.277	400r	50	3613.25	—	4	3643.526	5	1
3580.788	9	2	3613.45	7c	1	3643.725	25c	4c
3580.98	—	4h	3614.88	—	3h	3644.17	1h	—
3582.062	10c	2c	3615.500	30c	8c	3644.70	1h	—
3582.369	25	4	3615.971	4	1	3644.935	20	3
3583.095	2	—	3616.216	10	2	3645.360	9	1
3584.33	—	3h	3616.497	6	1	3645.94	1	6h
3584.357	1	—	3617.714	15	2	3646.118	4	—
3584.47	4	1	3618.043	1	—	3647.306	20c	4c
3584.972	100	10	3618.441	15	2	3647.724	7	1
3586.695	4	—	3618.907	15	4	3647.867	7	—
3586.75	—	50h	3619.207	10	—	3648.063	3d	1
3586.869	6	—	3619.514	30	200			
3587.400	9d	2	3619.729	15c	100c	3648.760	—	3h
3587.942	2	—	3620.57	—	6h	3648.84	1	—
3588.02	—	10h	3621.030	40	4	3649.854	60	5
3589.106	100	10	3621.92	1	—	3650.168	4	—
						3650.241	1	—
3589.356	100c	10c	3622.389	2	—			
3589.960	8	2	3622.49	—	3h	3650.31	2	—
3590.712	10c	3c	3622.621	4	—	3650.516	5	1
3590.904	10	2	3622.90	—	3h	3650.803	40c	4c
3591.197	6	40	3623.14	6c	—	3651.182	30	200
						3651.304	6	—
3591.52	2	—	3623.43	1	—			
3591.790	9	2	3624.357	7	2	3652.25	—	8h
3592.360	3	1	3625.169	15	3	3652.275	2	—
3593.45	1	—	3625.717	15	4	3653.276	4	1
3593.543	2	—	3627.870	8	1	3653.616	4	—
						3654.232	1	—
3593.966	80	9	3628.180	2	40			
3594.53	2	—	3628.921	4	—	3654.270	—	4
3596.361	2	—	3629.47	1	30	3654.430	10c	2
3597.260	15c	3c	3630.623	15	3	3655.975	20	4
3597.514	8	2	3630.700	5	1	3656.265	1	—
						3656.495	5h	1
3598.343	12d	2c	3631.338	4	1			
3599.279	20c	4c	3631.53	1h	—	3657.110	15	4
3599.635	20	5	3631.785	4	—	3657.254	4	1
3600.16	1	—	3633.006	15	2	3657.693	4	1
3600.678	3	1	3633.12	2	4	3657.897	8	2
						3658.604	4	—
3602.219	2	1	3633.318	6	100			
3602.561	60	10	3633.717	20	2	3658.648	4	—
3602.68	3	—	3633.894	—	5h	3657.750	7d	1h
3602.74	2	—	3634.03	1h	1h	3659.602	20c	300
3602.876	6	1	3634.452	15	—	3660.364	100	10
						3660.498	2	—
3603.435	10	2	3634.489	—	40			
3603.962	8	2	3634.604	5	—	3660.74	2	—
3604.072	8c	1c	3635.328	15	3	3661.680	10c	4
3604.643	7c	—	3635.468	6c	—	3662 051	15	3
3604.66	—	8h	3635.852	12c	2c			
3604.96	—	1	3636.457	2	—	3662.73	—	4
3606.272	8c	—	3636.64	2	1	3662.927	5	1
3606.35	—	2h	3636.959	30c	3c	3663.167	8c	—
3606.492	10d	2	3637.306	4	—	3663.313	2	—
3606.806	8	1	3637.545	20	3	3663.432	6	1

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
3663.751	—	60h	3692.518	1h	—	3722.548	—	40h
3664.467	—	2	3693.365	20	3	3722.942	20c	2c
3664.692	80	10	3693.667	4	—	3723.10	6	—
3664.822	7	2	3693.767	5	1	3723.44	1	30h
3665.157	10d	2	3694.669	20	3	3723.742	—	3h
3665.54	2	—	3694.792	—	10	3724.47	4	1
3666.534	15	4	3694.91	1	—	3724.96	4	1
3667.001	12c	3c	3695.38	1h	—	3725.195	20c	—
3667.665	10c	2	3695.90	8	100	3725.25	2	6
3667.760	8	2	3696.68	3	10h	3725.648	4c	1
3668.435	3	1	3697.024	6d	1	3726.235	250	20
3668.626	20	4	3697.155	1	—	3726.50	1	2
3669.009	40	6	3697.397	20	4	3726.56	2	4
3669.347	8h	2h	3697.850	200	20	3726.64	3	6
3669.736	20d	3	3698.79	—	2	3727.229	20	3
3670.05	1	20h	3698.893	3	—	3728.707	2	—
3671.372	12	2	3699.078	5	1	3729.613	7d	1
3671.735	6	1	3699.582	5	1	3730.853	1	—
3672.443	9	2	3699.928	30c	4c	3731.377	1	—
3672.580	8	2	3701.44	1	3	3731.534	8c	2c
3672.726	4	1	3701.713	—	3	3732.034	15	4
3673.227	8c	2c	3701.99	4	1	3732.702	5c	1
3674.469	4	1	3703.167	30c	6c	3733.344	15d	4
3674.691	15	2	3703.916	20c	5c	3733.622	15	2
3674.787	40c	6c	3704.137	40c	8c	3734.733	6	1
3675.17	5	1	3704.628	3	1	3735.931	2	—
3675.304	10	2	3705.602	10c	—	3736.32	4h	—
3676.307	20	—	3707.088	7c	—	3736.49	—	3h
3676.335	—	15	3707.803	10	—	3738.427	30	5
3677.084	20	3	3707.96	—	60c	3738.51	4	—
3677.771	15	2	3708.38	4c	—	3739.28	1	—
3677.905	4	—	3708.900	8	1	3739.80	300r	30
3678.063	2	40	3709.139	2	—	3740.537	8c	—
3678.70	10c	1	3709.29	—	100c	3740.726	10	200
3679.04	1	—	3709.422	25	3	3740.845	40	4
3679.61	—	10h	3709.736	6	—	3741.292	4	10
3680.857	5	1	3709.802	3	—	3741.553	1	—
3681.360	3	—	3709.947	2	—	3741.776	30c	4c
3681.57	—	2	3710.448	20c	4c	3741.99	2	—
3681.680	5	?	3711.343	60	7	3742.09	3	—
3681.690	—	6	3711.782	12	2	3742.393	200r	20
3682.13	1	—	3712.554	6	1	3743.18	1	—
3682.89	1	1	3713.018	300r	20	3744.007	40c	8c
3682.96	1	2	3713.356	—	25h	3744.279	4	1
3683.03	2	3	3713.72	2	50h	3745.476	6	1
3683.10	2	4	3713.819	20	2	3746.04	1	—
3683.973	5c	1	3714.59	—	2h	3746.904	25	5
3684.18	1	—	3714.852	5c	1	3747.841	3	—
3684.253	5	1	3715.196	4c	—	3748.00	1	3
3684.931	1	4	3715.974	6	1	3748.41	1	—
3685.128	10c	1c	3716.214	30c	2c	3748.557	20	5
3686.068	3	1	3717.01	40c	?	3749.248	1	—
3686.557	10	2	3717.06	20?	300	3749.415	1	—
3686.665	3	1	3717.31	1	—	3750.223	6	2
3687.440	8	1	3717.538	30	3	3750.517	5	1
3687.968	20c	200c	3718.524	6	1	3750.637	10	2
3688.187	10	50hl	3719.52	1h	—	3751.285	1	20
3688.698	15	2	3719.63	—	30c	3752.01	1	—
3688.81	4	—	3720.456	10	100	3752.08	1	—
3689.038	15	2	3721.277	6	1	3752.297	5	—
3689.27	—	3	3721.40	—	1	3752.723	9	1
3689.409	5	1	3721.517	10	1	3752.93	—	1
3691.174	4	30	3721.637	4	—	3753.171	40	4
3691.37	3	—	3722.170	4	—	3753.47	1	—
3692.178	—	5	3722.328	15	2	3754.428	2	—

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
3754.86	1*d*	—	3784.537	2	—	3816.342	15	3
3755.289	10	2	3784.73	1	—	3816.645	3*c*	—
3755.636	6*c*	1*c*	3784.88	3	5	3818.190	6*c*	—
3755.764	20	6	3785.384	3	1	3818.862	20	200
3755.940	4*c*	—	3786.10	6*c*	1	3819.148	40	5
3756.251	7	2	3786.227	10	2	3820.744	1	—
3757.02	4*c*	—	3787.064	150	20*c*	3821.201	12*c*	2*c*
3757.466	—	3*h*	3787.280	8*c*	1	3821.72	1	2
3757.60	—	1*h*	3787.480	15	2	3822.325	2	—
3757.62	2	—	3788.188	4	1	3822.956	4	1
						3823.135	6	1
3759.556	200*r*	20	3788.69	3*c*	—			
3760.646	12	2	3789.502	20	3	3823.255	3	—
3760.76	1	15*h*	3790.138	200*r*	30*c*	3824.00	—	4*h*
3761.130	30*c*	3*c*	3791.209	300*r*	40*c*	3824.17	—	5*h*
3761.32	—	2*h*	3791.446	8	2	3824.882	100	10
						3825.410	5	1
3762.064	2*c*	2*h*	3791.999	7*c*	2*c*			
3762.445	10*h*	2*h*	3792.79	—	30*h*	3826.574	3	—
3762.99	—	3*h*	3793.727	5*c*	1	3827.015	12	2
3763.13	1*h*	8*h*	3794.476	15	3	3827.43	1	—
3763.492	40	5	3795.182	2	—	3828.045	4	—
						3828.242	6	40
3763.730	4	1	3795.527	?	6*h*			
3764.115	25	4	3795.543	30*h*	?	3829.221	—	6*h*
3764.536	4	—	3796.440	20*c*	6*c*	3829.659	3	—
3764.641	—	5*h*	3796.599	12	3	3830.006	10	1
3765.074	40*c*	6*c*	3796.850	15*c*	6*c*	3830.601	—	20*c*
						3830.64	1*h*	—
3765.794	6	1	3798.127	300*r*	40*c*			
3766.140	30*c*	6*c*	3798.76	1	—	3830.820	1	—
3766.52	1	—	3799.486	5	1	3831.074	2	—
3766.62	1	—	3800.197	5	1	3831.198	6*d*	—
3767.421	5	1	3800.941	20	5*h*	3831.840	15	200
						3832.134	1	—
3769.145	20	3	3801.146	5	80			
3769.624	4	1	3801.302	20	3	3832.625	2	—
3769.983	15	2	3801.994	2*c*	—	3833.257	10*c*	2
3770.332	4	—	3802.19	1	—	3833.769	2	—
3770.66	—	30*h*	3802.480	4	—	3833.940	6	1
						3834.575	2	1
3770.71	12*c*	—	3802.555	5	—			
3770.870	20	3	3802.636	6	1	3835.176	40	6
3771.14	2	—	3802.928	400*r*	40*c*	3835.406	2	—
3771.79	3?	—	3803.65	1	—	3835.65	1	—
3771.848	40	6	3803.879	100	10	3836.260	3*c*	—
						3836.452	20	3
3772.721	3	—	3804.01	4	10			
3773.154	10	2	3804.204	10*c*	1	3836.738	5*c*	1
3773.22	2	—	3804.733	40	100	3837.077	12*c*	2*c*
3773.628	6	1	3805.23	—	1	3837.714	1	—
3774.39	4	1	3806.196	20	4	3837.995	4	—
						3838.072	2	—
3774.44	8	2	3806.631	10	2			
3774.98	1	—	3807.485	1	—	3838.42	2	—
3775.16	2	—	3807.95	2*c*	—	3840.16	1*h*	1*h*
3775.449	20	4	3808.10	—	4*h*	3841.666	—	10
3776.157	6*c*	1	3808.48	1	—	3841.820	30	4
						3842.709	20	3
3776.605	7	1	3808.70	1	1*h*			
3777.277	8	1	3808.95	1	—	3843.397	—	8*h*
3777.670	15*c*	3	3809.27	—	2*h*	3843.453	4	—
3778.50	2	—	3810.50	80*c*	30*c*	3843.927	10*c*	2*c*
3778.675	5	—	3810.88	3*c*	—	3844.090	12	3
						3845.079	2*c*	—
3779.03	1	—	3811.035	50	6			
3779.22	4	—	3811.41	—	5*h*	3845.29	—	2*h*
3779.57	1	20*h*	3811.44	1	—	3845.307	4*c*	—
3781.017	80	5	3813.01	5*c*	—	3845.900	40	6
3781.379	10	200	3813.416	1	—	3846.00	1	—
						3846.658	1	—
3781.90	1	—	3813.470	5	—			
3782.40	5*c*	—	3814.188	4	1	3848.46	1	—
3782.71	1	—	3814.71	2	—	3848.66	1	—
3783.53	1	—	3814.889	1	—	3849.744	6*c*	1
3783.844	20*c*	5*c*	3815.507	60*c*	10*c*	3850.056	—	3*h*
						3852.41	1	—

TABLE 2.—*Arc and spark spectra of columbium (Z=41)*—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
3852.63	1	6h	3878.965	20	3	3909.600	15	3
3853.096	4	1	3879.350	15c	200c	3909.665	4	1
3853.388	20	5	3879.644	7	—	3910.156	4	1
3853.59	4c	1	3880.122	1	—	3911.036	—	2h
3854.127	6	2	3880.40	1	—	3911.327	1	—
3854.698	9	2	3880.543	2	—	3911.587	1	—
3855.07	—	4h	3880.90	1	—	3912.084	2	—
3855.146	12	4	3881.407	1	—	3912.48	1d	—
3855.456	15	—	3881.541	1	—	3913.011	15	3
3855.500	—	50h	3881.85	—	4H	3913.15	8c	1c
3855.711	1	—	3882.660	8	2	3914.362	4	1
3856.683	6	?	3882.894	6	1	3914.692	150	30
3856.704	?	4	3883.140	80	15	3915.64	—	1h
3857.39	2	—	3884.519	3	1	3916.40	1d	—
3857.63	1h	—	3885.453	150c	30c	3917.014	4	1
3858.00	1	—	3885.686	100	20	3917.30	1	—
3858.953	40	6	3886.074	20	5	3917.584	2h	—
3859.237	4c	—	3886.664	6h	2h	3918.115	1	—
3860.48	1	—	3887.32	—	15c	3919.005	10	2
3860.694	1	—	3888.29	3	—	3919.163	15c	2
3860.860	12c	2c	3888.49	1	—	3919.718	6	100
3861.081	3c	—	3888.68	2	1	3920.198	100c	15c
3861.384	2	—	3889.14	1	—	3920.754	1	50h
3861.519	1	—	3889.440	1	—	3921.34	—	10h
3861.77	—	1	3889.64	8c	5c	3921.671	6	1
3862.926	20c	2c	3890.756	6	2	3922.280	4	1
3863.056	7	150	3891.302	60	10	3922.353	12	3
3863.383	50	5	3892.33	5	2	3923.80	4	1
3863.60	6c	—	3892.76	4	1	3924.02	—	2h
3863.78			3892.87	4	1	3924.474	12c	3
3864.111	1	—	3893.325	6	2	3924.995	40c	7c
3864.364	8	2	3893.733	40	7	3925.18	4c	1c
3864.698	1	—	3894.039	50	10	3925.53	3	1
3865.019	—	100h	3894.33	1d	—	3925.622	2	1
3865.041	10d	—	3894.564	—	5h	3926.203	1	—
3865.96	1	—	3894.70	10	2	3926.618	9	2
3866.24	4	1	3894.99	1	—	3926.903	1	—
3867.393	1	—	3895.36	1	—	3928.265	2	1
3867.918	50c	10c	3895.895	20	4	3929.296	30c	6
3868.570	8	2	3896.00	4	1	3930.022	—	10h
3868.829	9d	2	3896.31	1	—	3930.09	1	—
3869.23	2	—	3896.45	1	—	3930.81	—	2H
3869.586	1	—	3898.01	5	—	3931.460	8	2
3870.60	—	6h	3898.292	8	200	3931.590	—	2
3870.665	5	—	3898.563	20	3	3931.79	1	30h
3870.936	—	4	3898.94	4	1	3931.933	3h	—
3871.188	20c	4c	3899.24	15c	5c	3932.59	1	—
3871.76	5	1	3900.547	2	5	3933.013	6	1
3872.44	1h	—	3900.83	5	1	3933.392	8	2
3872.742	2c	1	3901.15	1	—	3934.142	12c	2c
3873.288	5	2	3901.73	1h	—	3934.405	20	3
3873.686	1h	—	3901.88	3	1	3934.64	2	1
3874.106	2	1	3902.39	1h	—	3934.81	2h	1h
3875.10	1	—	3902.829	4c	1	3935.441	20c	4c
3875.421	10d	2	3904.188	30c	10c	3936.02	4c	150c
3875.697	5	—	3904.83	2	1	3936.442	10	2
3875.77	20	3	3906.35	1h	—	3937.437	150	15c
3876.236	1	—	3906.900	12	4	3937.961	20	3
3876.376	1	—	3907.07	1d	—	3938.547	—	100h
3876.810	4	1	3907.34	1d	—	3939.26	3c	—
3876.964	20c	4c	3908.592	8	2	3939.77	1h	—
3877.557	60c	10c	3908.739	—	4	3940.074	1d	—
3878.082	1	—	3908.971	40	5	3940.790	2	—
3878.817	40	6	3909.231	3	—	3940.977	2	1
			3909.331	—	6h	3941.266	40c	6c

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
3941.611	4	1	3969.130	—	60h	4006.995	—	5c
3942.905	—	4h	3969.93	1h	—	4008.286	30	6
3943.663	60	10	3970.10	4h	1h	4009.533	1	—
3944.417	4h	1h	3970.650	12	3	4009.707	20	4
3944.730	2	—	3971.055	2	—	4010.10	—	3h
3944.90	2	—	3971.35	1	—	4010.581	1	—
3946.29	2	—	3971.679	—	30h	4012.056	6	—
3946.98	1	—	3971.852	20	3	4012.165	—	80h
3947.319	1	—	3971.932	15	2	4012.902	—	8h
3947.516	20	5	3972.25	—	2h	4013.101	4c	—
3947.922	4h	1h	3972.52	40c	15c	4013.268	20	5
3948.082	1	—	3973.624	20c	3	4013.942	4	2
3948.240	2	—	3973.87	2d	1h	4014.646	3	1
3948.433	—	5h	3975.20	6h	2h	4014.922	6c	3c
3949.326	8	1	3976.268	1	—	4015.748	3	1
3949.451	4c	60h	3976.52	1	200h	4016.06	—	3h
3949.70	—	1h	3976.677	15c	3c	4016.070	10h	—
3949.927	9	2	3977.940	20c	7c	4017.558	15	5
3950.966	4	1	3978.753	12	3	4017.793	2	1
3952.367	6	100h	3978.909	4	1	4018.995	—	4h
3953.015	4	—	3979.370	10	3	4019.13	2	1
3953.071	10	3	3980.483	60c	10c	4019.79	—	1
3953.524	2h	5h	3981.323	—	2h	4020.233	6	3
3954.18	1	—	3982.055	10c	3c	4021.016	4	2
3954.583	1d	—	3982.53	1h	—	4022.387	9c	3c
3955.38	1	—	3983.11	1h	—	4023.141	12	3
3955.55	1	3	3983.939	—	10h	4023.275	8	2
3955.680	20	2	3984.810	6	2	4023.41	2	—
3955.84	1	—	3985.074	4	2	4023.427	—	4
3955.882	—	30+N	3985.18	6c	2c	4024.26	2	1
3956.40	3c	—	3986.17	4c	—	4025.88	4	1
3956.626	3c	—	3988.158	20c	7c	4026.33	—	7h
3956.656	—	5h	3989.17	—	2h	4026.41	5c	—
3956.83	7	2	3989.52	1	1	4026.71	4	1
3957.724	1	—	3990.665	6	2	4026.93	1h	—
			3990.926	1	—			
3958.129	7c	2c	3991.677	40c	8c	4027.311	12	4
3959.144	3	1	3992.165	4	1	4027.972	15c	5c
3959.356	15c	4c	3992.55	1	—	4028.865	4d	1c
3959.54	2	—	3992.65	1	—	4029.223	6	2
3959.978	4	1				4029.824	1c	—
3960.636	4	1	3993.36	1	—	4030.348	10h	2h
3960.994	10c	3c	3993.48	—	3h	4030.864	—	3
3961.62	—	10h	3994.420	6	—	4031.317	—	6h
3962.154	4	—	3994.46	—	3h	4032.524	150	25
3962.163	—	8h	3995.588	3	—	4032.71	1	—
3963.03	1	—	3996.95	1	—	4033.195	40	6
3963.22	3h	—	3997.157	4	—	4034.178	1	—
3963.58	—	4h	3997.335	—	2	4034.527	6h	1
3963.60	3	—	3997.377	4h	—	4035.095	10	2
3964.26	1c	60h	3997.780	2d	—	4035.923	12	2
3964.512	1d	—	3998.23	4	1	4036.25	1	—
3964.665	7	2	3998.447	7	2	4037.356	4h	—
3965.53	2	—	3999.182	40	8	4037.67	—	40h
3965.692	40	6	3999.47	—	2	4038.172	8h	1h
3966.094	25	4	3999.71	2	8	4039.094	15	3
3966.246	100	?	3999.868	1	—	4039.530	60c	12c
3966.276	?	80h	4000.446	1	—	4039.804	1	—
3967.36	—	40h	4000.605	4c	80h	4040.468	8	3
3967.441	1	—	4001.135	15c	3c	4040.618	3	—
3967.61	1	—	4002.25	4h	2h	4041.39	1	—
3967.95	—	3h	4003.26	—	1h	4041.53	1	—
3968.11	1	—	4005.13	2	1	4042.572	10	2
3968.32	7c	1	4005.900	?	5	4043.169	10c	2c
3968.465	5c	—	4005.915	4	—	4044.103	25	5
3968.89	1	—	4006.05	4d	1h	4044.58	1	—

TABLE 2.—*Arc and spark spectra of columbium (Z=41)*—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
4044.712	12	3	4080.82	2h	—	4118.93	1h	—
4045.06	—	1h	4081.38	1h	—	4119.284	7	100h
4045.580	—	4h?	4082.14	1	—	4119.69	1h	—
4046.27	4h	1h	4082.65	—	5c	4119.74	—	10h
4047.964	—	3h	4083.776	5	1	4121.060	3c	1
4048.01	3	—	4084.177	10	2	4122.03	—	2h
4048.675	—	6h	4084.861	40	8	4122.804	15	5
4048.70	1	—	4084.951	4	—	4123.812	400	60
4048.95	3	1	4085.35	1	20h	4125.243	20c	5c
4049.759	20	6	4086.630	9	2	4125.573	12	3
4049.90	—	3	4087.048	6	1	4126.180	2	20h
4051.001	6	1	4087.583	1	—	4126.903	8c	3c
4051.285	1	—	4088.443	2	—	4127.458	12c	4
4051.513	25	5	4089.41	—	10h	4127.69	1	—
4052.132	6c	2c	4090.163	20	5	4127.93	1h	—
4053.161	6	2	4090.60	3c	—	4128.654	2	1
4054.23	1	—	4091.67	3	1	4129.000	4	2
4054.513	—	4h	4092.18	1h	—	4129.430	100c	15c
4055.186	8c	3c	4092.536	6h	1h	4129.931	150c	30c
4055.426	2	1	4093.926	6	2	4131.53	6	4c
4055.854	4c	2c	4094.095	6	2	4131.60	3	—
4056.941	8	2	4094.31	1	—	4131.74	2	—
4057.267	6c	2c	4095.082	8h	1h	4132.175	3c	1
4058.933	2,000c	200c	4095.553	7	2	4132.67	1h	—
4059.498	40	4	4095.930	6h	20h	4133.40	5h	—
4059.68	2	10	4096.28	—	2h	4134.33	1	—
4059.83	—	2	4096.314	5h	—	4134.592	30	7
4059.85	5	—	4097.63	10c	1	4134.985	6	2
4060.32	10	4c	4097.93	—	2	4135.423	10	3
4060.37	4		4098.220	10	2	4135.57	4	1
4060.800	40c	10c	4098.87	5h	—	4136.67	1c	—
4061.255	9	3	4099.067	30	6	4136.72	—	3h
4061.427	4	1	4100.11	1	—	4137.090	200	30
4061.542	10	2	4100.30	3?	—	4137.590	12c	4c
4061.98	4	60h	4100.389	80	15	4138.300	10c	2
4062.21	2	—	4100.918	600c	100c	4138.46	2	10h
4063.09	1h	—	4101.38	—	3h	4138.91	—	2
4063.734	1	10h	4103.43	1h	—	4139.088	6	2
4064.058	—	15h	4103.74	3	—	4139.430	90c	10c
4064.802	10	3	4104.165	4	50h	4139.702	400c	50c
4065.738	1	—	4104.71	1	—	4140.43	2	—
4066.120	12	4	4105.47	1	—	4140.59	—	6h
4067.159	15	4	4106.173	12	3	4141.32	4	—
4068.258	40c	15c	4106.778	6	1	4142.243	9	3
4068.712	—	5	4106.99	—	2h	4142.80	2	—
4069.16	2h	—	4107.05	3c	—	4143.201	80c	10c
4070.040	6c	—	4107.67	1h	—	4143.58	4c	—
4070.965	20	4	4108.71	3	—	4143.931	5c	1c
4071.49	1	—	4109.00	—	4h	4144.419	1	—
4071.59	2	—	4109.88	4	1	4145.155	3c	1c
4072.064	5	15	4110.12	2	—	4146.000	10	2
4072.13	2	—	4110.32	2	20h	4146.35	1	—
4073.09	2h	20h	4110.81	—	8h	4146.598	1	—
4073.513	6	1	4112.130	20c	8c	4146.989	—	4c
4073.641	6	1	4112.49	1	—	4147.184	25c	6c
4074.110	—	1	4113.348	6	3	4148.321	6	2
4074.66	—	2	4113.941	25	7	4148.550	—	4c
4076.09	8	1	4114.155	6	2	4148.735	15	3
4077.09	15c	3c	4114.56	—	10h	4149.721	4	1
4077.405	4	1	4115.597	—	10h	4150.124	100	25
4078.345	6	1	4115.90	1h	—	4152.040	20c	4c
4078.60	7c	—	4116.274	2	1	4152.575	500	80c
4079.10	—	10c	4116.401	5	1	4154.826	6	2
4079.34	—	6h	4116.895	50	10c	4155.36	4c	2h
4079.726	1,000c	100c	4117.824	2	1	4156.678	4c	100c

TABLE 2.—*Arc and spark spectra of columbium (Z=41)*—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
4157.008	2c	—	4198.370	10c	3	4248.07	1*h*	—
4158.007	20	5	4198.510	30	5	4248.658	8	2
4158.820	1	—	4198.672	1	—	4248.961	3	1
4159.49	1	1	4198.847	10	2	4249.457	20	6
4160.806	8	2	4198.90	2	—	4252.977	80c	20c
4161.252	20c	7c	4199.189	6	—	4253.695	50c	10c
4161.884	3c	1c	4199.23	—	8*h*	4254.05	—	5*h*
4162.817	12c	4c	4200.993	7	2	4254.392	3c	30c
4163.474	40	6	4201.519	40	10	4254.693	30	5
4163.658	250	50	4202.013	6	1	4255.439	60c	20c
4164.661	300	60	4202.50	1	—	4255.943	20c	6c
4165.330	4c	—	4202.880	—	2*h*	4256.303	4	2
4165.850	20	5	4203.08	1	—	4257.853	5	2
4166.045	6	2	4203.415	7	2	4258.120	1	—
4167.44	3c	1*h*	4203.732	1	—	4258.917	12c	4
4168.122	250c	50c	4203.825	1	—	4259.206	2	1
4169.365	30c	6c	4204.322	10	2	4260.661	5	2
4169.72	2	—	4205.308	120	30c	4261.717	20c	5c
4170.909	3c	—	4206.127	10	3	4262.056	100	20
4172.34	1c	—	4206.70	1*h*	—	4263.164	1*h*	—
4172.54	—	6*h*	4208.156	30	8	4264.612	4	2
4173.955	12c	4	4209.708	1	—	4264.90	2	1
4174.047	3	—	4212.042	12	4	4265.83	1	—
4174.342	15	4	4212.535	15	5	4266.020	50	10
4174.894	5	1	4213.256	10c	3c	4266.27	—	8*h*
4175.506	1*h*	—	4213.463	10c	3c	4266.835	1	—
4175.76	2c	—	4214.70	?	10c	4267.65	—	20*h*
4176.166	1	—	4214.732	100c	?	4268.070	1	—
4176.78	1*h*	—	4214.81	?	20	4268.667	15	5
4177.435	4	1	4215.13	1*h*	—	4269.92	—	5*h*
4177.554	1c	—	4216.228	4	50*h*	4270.691	50c	20c
4177.873	—	5c	4217.946	150c	25	4272.027	4c	2c
4178.088	2	—	4218.53	1	30*h*	4272.972	8	4
4178.40	1	6*h*	4219.390	1	—	4273.357	5	3
4179.233	2c	—	4220.598	2	15*h*	4274.692	20	3
4179.763	12	4*dl*	4222.676	9	2	4274.87	1	12*h*
4179.826	4*f*		4224.690	5c	2	4277.500	20	5
4180.992	1	—	4225.177	2	1	4278.18	1	—
4181.048	2	—	4225.85	1	—	4279.49	20	6*d*
4181.341	15	3	4226.190	6	?	4279.53	5*f*	
4181.52	—	2	4226.22	?	3c	4279.707	8	3
4181.784	6	1	4226.245	6	—	4280.38	1	—
4183.39	—	7*h*	4226.528	8c	3	4280.586	30	10
4183.910	2	—	4226.96	2c	1	4281.120	2	1
4184.440	50c	15c	4227.514	8	3	4282.968	3	1
4185.54	1	50*h*	4228.726	8c	1c	4283.055	3	1
4185.66	3	—	4229.154	100c	30c	4283.906	1	—
4186.104	15	4	4229.570	1*h*	—	4284.14	1*h*	—
4188.098	3c	—	4229.832	25	5	4284.683	1*h*	—
4189.250	3c	—	4230.320	20	5	4285.31	1	—
4189.312	—	2	4231.624	1	—	4285.842	2	1
4189.47	—	1	4231.954	25	5	4286.216	15	5
4189.59	3c	—	4233.160	1	—	4286.987	60	15
4189.997	12	3	4236.40	1	—	4288.12	1	—
4190.655	20c	4c	4236.998	4c	1	4288.299	6	2
4190.889	150c	25c	4237.814	12c	13	4288.429	1	—
4192.065	100c	15c	4238.118	1	—	4289.443	30	8
4193.42	1	—	4241.077	4	1	4289.85	4	—
4193.80	—	10*h*	4241.453	12	3	4290.35	—	2*h*
4193.828	10c	—	4242.637	20c	6	4291.195	25	6
4195.096	80	20	4244.26	1	—	4291.344	1	—
4195.515	4	1	4245.15	1	—	4292.035	20c	5c
4195.660	15	4	4246.293	20	6	4292.480	40c	15c
4196.948	9c	2c	4246.628	1	—	4293.86	—	—
4197.615	7c	2	4247.689	4c	2	4294.33	1	4c

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
4295.253	1	—	4337.561	12c	3c	4396.77	—	3h
4295.620	15	5	4338.696	6	2	4397.036	10	3
4295.71	—	4	4338.808	2	1	4398.55	—	7h
4296.159	20c	8c	4339.95	1	—	4400.368	10c	4c
4296.44	—	2h	4342.460	7	2	4400.832	10	2
4296.726	1	—	4342.818	25	7	4401.172	2	50h
4297.526	1	—	4345.20	9	6c	4402.056	7c	3
4297.920	6	2	4345.34	10		4403.925	2	1
4298.101	2	—	4345.518	6c	3c	4404.74	1	—
4298.43	1h	—	4346.120	10	4	4406.546	10c	3
4298.699	1	—	4346.43	3*Bl*	—	4407.26	1	—
4299.45	—	3h	4347.312	8c	2	4407.78	—	5h
4299.596	100	20	4348.244	1c	6h	4408.729	1h	10h
4300.53	—	10h	4348.652	40c	6c	4410.214	60	15
4300.57	1	—	4349.026	30	5	4410.674	1	—
4300.989	100	15	4350.302	9	3	4410.882	2	1
4301.204	4	2	4351.573	40	10	4411.526	15	5
4301.678	1	—	4351.88	1	—	4412.184	5	2
4302.435	3	1	4352.243	2c	—	4413.000	2	—
4302.91	1	8h	4352.52	1	—	4413.15	—	6h
4303.875	9c	3	4352.66	2	—	4414.879	8c	—
4304.659	4c	2c	4353.266	20	4	4415.080	2	—
4306.283	15	4	4354.006	3	2	4416.406	6	2
4306.70	1	—	4354.188	6	3	4416.879	2c	—
4306.99	—	7h	4354.784	4	2	4418.166	1	—
4307.233	2c	—	4355.245	5c	2c	4419.448	40	10
4308.117	15c	6c	4356.847	7	3	4419.839	10	3
4308.692	20c	5c	4359.865	40c	20c	4420.455	10	3
4309.564	20	6	4360.504	5c	4h	4420.637	30c	8c
4310.826	4	2	4361.34	—	3h	4421.305	2	—
4311.27	50c	30c	4361.656	9	3	4421.660	—	20h
4311.37	20		4367.387	2	20h	4423.868	6c	2
4311.695	15	5	4367.966	7	100h	4424.66	—	30h
4312.121	4	1	4368.434	50	10c	4426.27	—	2h
4312.454	25	6	4369.618	8	2	4426.690	20	4
4312.70	—	5h	4370.361	15	4	4427.05	—	10h
4312.88	1	1	4372.645	1c	40h	4427.683	—	4h
4313.887	10c	5	4374.60	—	3h	4427.866	1	—
4314.262	3	1	4374.789	12c	3c	4428.576	2	—
4315.144	1	—	4375.246	6	3	4429.446	20c	6c
4316.476	12c	3c	4376.707	4	2	4430.029	1	—
4316.756	1	—	4377.20	2	2	4432.912	2c	—
4317.72	—	40h	4377.823	5	2	4433.496	3c	1
4318.010	10	2	4377.958	30c	10c	4433.895	1	—
4319.147	3	1	4379.394	2	1	4434.997	3	1
4319.52	1	—	4379.525	12	3	4435.919	3	1
4320.800	6	2	4380.664	4c	2	4436.712	5	2
4321.49	1	50h	4381.114	10c	5c	4437.218	100c	60c
4321.88	3c	1	4381.98	1	—	4437.918	7c	4c
4322.148	1	—	4382.496	7	3	4439.38	1c	—
4322.765	1h	—	4382.856	9c	3c	4440.435	5	2
4323.466	8	3	4383.70	1	1	4441.61	3c	1
4326.320	100c	30c	4384.870	15c	5	4441.802	10c	2c
4326.540	9	3	4385.790	1	—	4442.41	—	3h
4327.385	25c	8c	4386.302	4	2	4443.00	—	5h
4328.428	30c	9c	4387.743	15	4	4443.05	1	—
4329.47	4c	2c	4388.357	30	8	4443.302	2	1
4329.732	20c	5c	4389.496	2	1	4443.80	2	—
4331.252	2	—	4390.63	1	3h	4444.26	1	2h
4331.371	60	15	4391.214	7	3	4444.92	1	—
4332.17	1	—	4391.59	4c	2h	4445.17	—	2h
4332.428	5	2	4392.692	30	10	4445.843	15c	3
4334.23	2h	1	4394.229	3	1	4446.181	12	3
4335.011	1	—	4394.58	1	1	4446.232	4	—
4336.548	6	2	4395.61	1	—	4447.184	100	10

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
4447.737	—	10h	4515.93	—	6h	4575.372	12	5
4448.06	2	—	4516.914	5	2	4578.52	2h	2h
4448.769	6	2	4519.02	2	1	4579.446	6	150h
4449.912	2	50h	4520.40	2	1	4580.50	—	5h
4454.68	3c	2c	4520.836	5	2	4581.623	100	50c
4456.331	4c	2c	4521.132	1	—	4582.283	20	6
4456.800	30	6	4521.703	1	—	4582.87	2	1
4457.424	50	10	4522.21	—	30h	4583.132	4	2
4458.117	15	5	4522.545	6	2	4583.49	7c	3d
4459.01	1	—	4523.409	200	30	4584.10	—	6h
4459.671	2	1	4523.727	5	2	4584.849	6c	2d
4460.17	—	12c	4524.127	20	5	4586.31	2	—
4460.203	15c	—	4526.425	1	—	4586.73	—	2h
4460.423	20c	8	4526.52	—	3h	4589.00	—	30h
4461.49	1	—	4527.648	5	50h	4592.42	4	1
4461.92	—	2h	4529.250	2	—	4593.79	—	50h
4464.151	20	6	4529.415	6	2	4594.48	1h	1h
4465.232	4	1	4530.43	1	—	4594.97	1	—
4465.926	7	2	4532.47	3c	2c	4598.01	—	1h
4466.198	2	1	4532.76	2	1	4599.475	10c	5c
4466.421	5	2	4523.28	—	2h	4600.22	30	15
4467.92	—	20h+O	4533.92	3d	2d	4600.95	2	1
4468.54	1	—	4534.715	2	1	4602.48	2	1
4468.644	2	1	4535.69	—	8c	4602.864	7	3
4469.322	10	3	4537.33	2	1	4603.797	5c	2c
4469.714	40c	12c	4537.59	5c	2h	4605.649	4	3
4471.292	50c	20c	4540.10	4c	—	4606.760	200	80
4472.536	40c	10c	4541.35	2	1	4607.28	1	—
4472.874	2	1	4541.863	4	2	4608.04	—	2
4474.66	—	7h	4542.797	12c	4c	4608.567	9c	4
4475.278	6	3	4543.60	1	1	4609.90	1	8h
4475.95	4	2	4543.72	4	2	4610.106	4	1
4476.498	4c	2c	4546.820	120	30	4610.698	7c	3c
4477.585	3	2	4547.847	8	3	4612.02	2	2
4478.118	3c	2c	4548.71	—	10h	4612.108	8	4
4480.362	4	2	4550.10	—	50h	4612.465	4	3
4481.01	—	2h	4550.65	3	2	4614.740	5c	3
4481.445	8	3	4551.03	4d	2	4616.162	50	20
4482.877	4	2	4551.52	3	1	4617.555	—	4c
4484.76	2	—	4551.909	5	2	4618.41	—	2h
4484.85	1	—	4553.839	30	10	4619.04	—	1
4485.97	—	2h	4554.422	1	—	4619.42	3	2
4487.358	1	1	4555.556	3	1	4620.02	2	2
4489.33	2	1	4556.68	—	3h	4622.338	6	3
4489.71	—	2	4556.854	15	7	4623.43	—	1
4490.35	2	1	4559.429	5	3	4623.98	—	1
4491.041	4	2	4560.88	1h	1h	4624.576	4c	2c
4491.913	2	1	4561.47	4c	2h	4625.335	1	2
4492.962	3	200h	4562.33	2	2	4625.955	2	2
4494.845	10	4	4564.205	6c	3c	4627.03	1	2
4495.46	—	8c	4564.530	60	20	4627.477	7d	6h
4497.25	5	2	4566.26	—	3h	4628.66	—	2
4498.16	—	4c	4566.57	2	1h	4630.115	100	50
4499.805	20	8	4567.11	4	2	4630.30	3h	—
4500.50	2c	2c	4567.34	2h	2c	4631.976	3	2
4501.74	1	1	4567.67	1	—	4632.25	1	1
4503.040	50	20	4569.15	6c	2c	4632.85	—	4
4503.416	10	4	4569.49	4	3	4633.21	1	3
4507.24	1	—	4570.02	2h	1h	4633.80	5c	2
4508.409	15	5	4570.960	6	3	4636.728	—	2h
4510.61	5Bl	—	4571.89	1	—	4637.575	—	20h
4511.084	30c	10	4573.077	200c	60c	4638.105	10	6d
4512.130	7	3	4574.338	7	3	4638.17	4	
4512.65	2c	2c	4574.572	2	1	4640.248	5	2
4513.44	3c	2c	4574.848	25c	10c	4642.46	3	—

TABLE 2.—*Arc and spark spectra of columbium (Z=41)*—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
4643.315	10	3	4695.93	2	2	4772.79	5c	2c
4643.682	10c	1	4696.62	—	1h	4773.24	20c	9c
4643.86	5c	3	4697.468	30	15c	4773.80	—	7
4645.405	2	1	4697.752	4	2	4776.07	2	1
4645.84	4c	2	4698.138	—	1	4776.224	2	1
4646.952	20c	10c	4698.506	—	1	4777.62	6c	3c
4647.54	2	2	4699.58	—	150	4780.07	1	1
4648.949	100	40	4700.30	—	1	4780.98	5c	—
4649.255	40	20	4700.91	—	2c	4782.17	1	1
4649.622	2	—	4701.49	—	1	4782.44	—	1
4650.01	1	—	4702.02	5	4c	4782.948	4	2
4652.08	3	—	4702.70	—	1	4784.30	5c	2c
4652.19	—	10h	4703.32	—	1h	4785.607	7	3
4653.802	2	1	4703.92	4?	3	4787.56	1	1
4654.89	1	—	4704.60	—	1	4787.73	3	2
4655.30	—	6h	4705.09	4	3	4789.80	—	8h?
4655.953	1	1	4706.132	100c	70c	4789.959	25	100
4658.186	12	4	4707.103	5d	2	4790.58	6d	3c
4660.41	—	10h	4708.284	150	100	4790.902	9	4
4660.70	3h	1	4711.872	6d	3c	4791.48	—	4h
4660.98	5h	2	4713.038	9c	4c	4793.07	5c	2c
4662.89	4c	1	4713.495	80	20	4794.59	—	1
4663.131	2	1	4715.819	20	8	4798.818	2	1
4663.831	100	40	4717.52	—	2c	4800.07	—	2
4663.97	4?	2	4718.024	8	5	4802.442	9	3
4664.366	5	2	4720.10	2	2	4803.83	—	1
4665.333	10	3	4723.146	3	2	4805.16	—	1
4665.60	—	6h	4723.795	15c	7c	4805.61	3	2
4666.251	100	50	4724.48	2	1	4806.63	—	1
4666.630	6c	4c	4726.09	—	1h	4807.052	10	5
4666.96	—	1h	4726.77	4d	2c	4809.03	4c	4d
4667.224	50	20	4727.320	10c	5	4809.12	4	
4668.232	6	2	4730.312	20	6	4809.357	30	12
4668.966	3c	—	4733.483	30c	10c	4810.584	100c	50c
4669.08	—	4h	4733.885	60c	40c	4811.287	12c	5c
4669.32	2c	2h	4735.04	—	2	4812.12	2	1
4669.868	10	5	4735.339	10	3	4814.98	2	1
4670.104	1	100	4736.49	20c	8c	4816.375	80c	40c
4670.87	3c	2c	4740.426	2	1	4820.07	1	1
4672.097	200c	100c	4740.61	15c	5c	4821.11	3	1
4673.589	12c	3c	4742.072	3	1	4822.93	—	2
4674.378	2	1	4742.43	4c	2c	4824.17	1	12h
4675.371	150	60	4743.839	15	5	4824.954	6c	3c
4676.29	1	—	4744.622	30	20	4826.50	1	—
4677.072	2	—	4745.020	10c	3c	4826.97	1	1
4678.44	10	8d	4746.987	9c	3	4829.302	30	15
4678.51	12		4748.04	3h	1	4830.69	2	1
4680.890	4c	3c	4748.84	3c	2c	4832.21	3	1
4681.53	1	3c	4749.706	200c	150c	4833.362	40	15
4681.66	3		4750.74	5	1	4835.56	—	1
4681.997	2	1	4751.44	20	8	4836.44	—	2h
4682.664	10c	4c	4752.10	5h	1h	4837.615	15	5
4682.984	7	3	4752.86	1	1	4837.98	20c	8c
4683.68		1	4753.48	3d	—	4840.28	1	1c
4685.133	100	40	4754.957	5	2	4840.39	1	
4685.518	9	3	4755.318	10c	6c	4842.139	20c	8c
4685.925	9	3	4756.538	4	2	4845.170	20	8
4687.19	1h	—	4757.22	—	3c	4845.46	2	1
4687.790	3	2	4758.12	2c	2c	4847.39	3h	2h
4688.49	4B?	1	4766.53	6	3	4848.02	—	1
4688.83	5c	—	4766.80	30c	20c	4848.359	100c	70c
4689.162	10	2	4767.07	5	2	4849.35	2	1
4692.255	3	2c	4768.23	—	3h	4851.881	7c	3
4694.50	15c	6c	4771.852	7	3	4852.101	—	4
4695.46	20c	10c	4772.20	1	1	4852.273	6	3

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
4853.89	1	1h	4976.75	—	1	5116.741	5	2
4854.738	—	3h	4985.18	1	1	5118.065	3	1
4854.960	—	3h	4988.972	40	15	5120.298	20	8
4857.31	1h	1h	4991.38	1	—	5120.492	—	2h
4858.46	1	2h	4992.466	6c	2	5121.801	12	4
4860.994	2	2	4993.232	3	1	5124.694	4c	2c
4865.99	1	12c	4993.83	1	2	5127.662	9	3
4866.842	12c	4c	4994.303	12	7	5128.278	2	1
4868.99	20	10	4997.880	15	6	5129.74	1	1
4870.32	1	1	5000.712	4	2	5133.338	7	2
4872.505	5	2	5000.958	20c	10c	5134.752	40	15
4878.496	5	2	5002.247	12	6	5135.47	2c	1c
4879.20	1	1	5006.22	—	2	5137.398	3c	2c
4880.714	8c	3c	5008.039	6	3	5140.578	8	3
4881.68	2	1	5011.750	4	2	5140.68	3	1
4885.765	5	2	5013.275	9c	3	5145.65	1	1
4889.551	7c	3c	5017.363	3c	1c	5146.03	1c	1c
4889.809	3	1	5017.743	40	20c	5147.537	12c	5c
4890.730	25	15	5019.512	8c	3c	5147.94	—	4h
4891.07	—	2	5026.362	20	10c	5149.62	1	1
4892.50	12c	6c	5028.65	2	1	5150.636	7c	3
4893.885	—	15h	5029.67	3	1	5152.623	12c	8c
4895.574	10c	4c	5030.130	7	3	5153.028	6	3
4897.51	2	2	5031.884	5c	2	5153.63	2	1
4898.491	4	3	5035.99	6c	3c	5157.14	2	1
4900.786	20	7	5037.89	1c?	—	5157.486	3	2
4903.02	1h	1h	5039.032	40	15	5158.030	2	1
4904.534	25	5	5041.77	1	1	5160.335	50	20
4908.331	3c	2c	5043.030	3c	2	5161.63	1	1
4908.716	7c	3c	5043.47	1h	1h	5164.368	40c	15c
4910.948	30	15	5043.985	5	2	5165.368	—	4h
4915.31	4B?	—	5046.756	3	1	5166.96	1	1
4915.842	7	2	5047.956	12c	4	5167.37	1	1
4916.392	15c	6c	5049.91	2	1	5174.198	3	2
4917.76	1	1	5051.59	1	1	5174.569	2	2
4920.75	3h	1	5054.22	1	1	5178.209	3c	1
4921.07	1	1	5054.671	8	3	5180.306	50	15
4923.742	—	2h	5055.62	2c	1	5183.31	—	1h
4924.862	6c	3	5057.990	40	15	5183.81	1h	1h
4928.909	15	6	5059.353	10	4	5186.987	15	4
4929.556	5	2	5060.99	1c?	—	5189.198	20	9
4932.140	2	1	5064.45	3c	2c	5193.078	40c	15c
4933.20	2?	3c	5065.256	20	8	5193.454	5	2
4936.66	—	2h	5071.66	4c	2c	5195.839	20	8
4937.45	—	1h	5072.56	3c	1c	5197.37	2c	1
4941.513	9	3	5075.97	5c	2	5201.089	3	1
4941.905	2h	—	5077.391	7c	2	5201.938	3	2
4942.00	—	4h	5078.959	150	60	5203.224	10	4
4945.432	12c	5c	5079.314	3	1	5204.03	3c	2c
4949.439	—	3h	5082.31	2	1	5205.132	8	3
4950.07	—	1c?	5084.90	5c	3c	5207.65	2	1
4951.54	1	1	5086.83	3h	1	5210.26	2	1
4953.124	7	3	5088.82	9c	3c	5211.239	4c	3c
4956.60	3c	1c	5094.342	3		5215.65	—	2h
4957.393	8c	3c	5094.416	3	3c	5218.46	3c	2
4957.74	—	8h	5094.485	3		5219.09	15c	8c
4960.434	—	1	5095.14	3	1	5225.156	12	5
4962.950	5h	2	5095.298	80	25c	5229.37	3	1
4963.189	7	2	5095.535	7c	2c	5229.94	2	1
4965.375	25c	12c	5096.57	2	1	5232.813	25	10
4967.777	30c	20c	5097.77	5c	1	5235.096	3c	2
4969.44	—	2	5098.87	3	1	5236.32	1	2
4971.917	10c	3c	5100.162	30	10	5236.837	4	3
4973.138	15	7	5102.38	4c	2c	5237.34	—	5c
4975.135	10c	4c	5110.910	6c	2c	5237.37	7	—

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
5237.47	9	3	5363.28	1	—	5483.48	8	3
5240.39	5c	2	5365.88	1	100h	5484.58	1	1
5241.50	4c	2	5368.390	4	2	5487.60	1	200
5247.38	10c	4c	5371.111	4	1	5491.062	4	2
5251.62	15c	10c	5375.262	8	4	5494.09	5h	3h
5251.81	10c							
5253.028	10	4	5375.916	3c	1c	5499.53	7	2
5253.926	15	6	5376.722	2	1	5499.87	1	1
5255.52	1c	2c	5377.79	3c	1c	5500.53	1	1
5260.13	3c	2c	5380.705	4c	1c	5501.759	5	2
			5381.326	10	5	5502.45	1h	1h
5260.849	2c	1						
5269.910	6	3	5382.942	3	1	5504.58	30c	10c
5271.526	60c	30c	5383.87	—	10*H*	5504.79	2	1
5272.48	5	2	5383.99	1	—	5506.74	1c	1h
5273.486	—	5h	5388.300	6	2	5507.86	1	1h
			5393.98	—	10*H*	5509.13	7	3
5276.196	50c	20c						
5277.42	3	1	5394.36	3c	1	5510.19	—	3h
5278.542	5	2	5395.483	2	—	5510.69	2h	1
5279.418	8c	3c	5395.849	5	3	5511.22	4c	2h
5281.62	1	2	5396.33	7c	4c	5512.81	15c	6c
			5400.56	1	—	5517.39	5	3
5285.240	20c	10c						
5285.43	2	—	5402.49	2	1	5521.89	3	1
5287.08	2	—	5403.06	2	1	5523.57	30	15
5293.292	5c	2c	5404.427	2	1	5532.59	4	2
5294.47	2	—	5408.92	—	20*H*	5538.736	3	1
			5409.43	2	1	5540.20	2h	1h
5296.34	8c	3c						
5298.108	4	2	5411.235	8	4	5541.461	0	3
5298.95	4	2	5416.292	6c	3	5545.52	2c	—
5301.434	2	1	5422.42	20	10	5545.63	—	100
5303.27	3	—	5423.48	—	2c	5546.35	—	2
			5427.82	1	1	5549.60	8c	?
5306.380	4c	1c						
5306.606	3	1	5431.25	12d	6c	5549.62	?	20*H*
5306.97	2	1	5431.77	1	—	5550.18	2	—
5314.283	3c	—	5432.478	2	1	5551.34	60	30
5315.543	10	5	5433.54	—	50*H*	5552.33	5	2
			5434.46	1	—	5553.115	4	2
5317.001	4	2						
5317.804	5c	3c	5437.265	50	30	5559.34	1	1
5318.597	50	30	5437.998	2c	1c	5562.99	15	10
5319.485	15	6	5439.78	—	50*H*	5566.12	2	1
5320.205	3	1	5443.08	4c	3	5571.41	10c	?
			5443.77	1c	1	5571.43	?	20*H*
5321.323	4	2						
5321.659	2	1	5445.15	4	2	5572.00	—	10*H*
5321.917	2	1	5448.306	8	5	5572.52	2	2h
5323.354	3	1	5452.79	2	1	5576.16	15c	6c
5329.341	3c	1	5455.03	—	30	5577.06	1c	1c
			5456.19	6	4	5578.07	4c	2
5331.19	—	10h						
5334.27	1c	—	5457.60	—	30*H*	5578.28	15	10
5334.854	30c	15c	5457.66	3	—	5586.99	30	10
5336.797	6	3	5458.043	10c	6	5590.05	—	2*H*
5337.872	4c	2c	5459.51	—	5*H*?	5590.43	1	1
			5460.935	4c	2c	5590.95	15c	7h
5339.89	1	1	5462.03	1	—	5594.87	6c	3c
5340.793	10	5	5462.98	1	—	5595.72	—	20*H*
5343.602	8c	4c	5463.95	1	—	5596.87	5h	2h
5344.160	200c	100c	5466.90	2	1	5599.57	10c	4h
5345.55	2c	—	5467.41	3	1	5603.51	30	10
5350.723	100c	60c	5468.10	9	5	5603.93	7	3
5351.022	6	3	5469.55	6c	2	5606.36	2	1
5353.283	5	3	5471.90	2c	1	5612.30	—	20*H*
5355.086	3c	1	5476.07	5c	3	5616.27	1h	—
5355.300	5	3	5477.33	1	1	5616.99	2c	1c
5355.683	9	4	5477.96	1	—	5618.69	3	1
5356.84	—	15h	5478.74	3	1	5619.78	1h	—
5359.183	7	3	5479.205	4c	2	5622.09	1	—
5362.003	6	2	5481.002	15	8	5628.25	10c	3
5363.075	4	8?	5483.08	5c	2	5629.17	40	20

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
5629.81	6c	2	5794.24	20	10	5971.25	5c	3h
5633.64	2c	2c	5801.01	2c	—	5973.26	—	8h
5635.42	20c	?	5801.78	1h	1h	5979.55	2c?	2h
5635.48	?	20*H*	5804.02	30*d*	15	5983.21	100	50
5642.10	80	40	5804.65	4c	1h	5986.08	30	20
5644.66	—	2h	5805.91	1	—	5986.61	5	2
5645.30	10	4	5809.08	1	—	5992.32	2h	1h
5648.40	3c	1c	5810.68	5c	2c	5994.84	2	1
5654.13	5	2	5811.89	3	4	5995.94	1	1
5662.04	1	—	5815.316	15c	6c	5997.86	50c	25c
5664.70	100	50	5819.415	80	50	6000.25	—	6h
5665.63	120	60	5820.01	2	1	6018.96	2	2
5666.86	9	—	5820.61	20c	10c	6021.41	2h	2h
5671.09	60c	40c	5825.41	3	1h	6022.41	—	2*H*
5671.90	50	20	5828.85	—	4h	6022.50	1	—
5675.942	3	—	5834.40	2	1	6025.29	2	—
5677.453	10	4	5834.88	40	25	6028.73	5c	1h
5684.45	5c	2c	5838.13	15c	6c	6029.74	12	5
5690.78	—	3h	5838.61	100c	60c	6031.83	10	5
5693.07	8	3	5839.17	2	2	6039.95	—	15h
5697.89	5	5c	5842.47	30	15	6041.96	4	2
5698.01	4		5846.10	20c	10c	6045.49	20	10
5706.16	15	8	5848.34	1	—	6047.46	2h	1h
5706.47	50	20	5850.67	2	1	6048.71	10c	5
5708.46	2	1	5851.94	1	—	6052.31	2	1
5709.33	15	6	5852.79	6	3	6052.59	1	—
5712.02	2	1	5855.72	6	2	6054.42	1	1
5713.44	2	1	5856.70	5	2	6056.64	12c	6
5713.79	5c	2c	5858.81	2h	—	6062.17	—	5h
5715.58	6	3	5862.12	4	2	6065.68	1	—
5716.34	30	20	5863.21	2c	1c	6067.81	4	2
5719.62	1	—	5864.12	1	—	6072.60	1	1
5722.70	4	1	5864.43	2	1	6073.02	1	1
5725.66	9	5	5864.94	6	3	6083.55	6	2
5726.13	1h	1c	5866.45	80	40	6091.80	—	5h
5729.185	80	30	5868.89	6	2	6103.49	4c	2h
5730.32	1	1	5872.36	2	2c	6105.30	2	1
5731.99	1h	1h	5872.56	2		6107.69	9	5
5734.35	1c	?	5874.68	40c	20c	6110.94	6	3
5734.43	?	3c	5875.24	7c	3	6118.10	4c	1
5737.35	7	3	5876.30	8c	5c	6119.68	—	5h
5738.19	6	2	5877.78	20	10	6119.80	6*Bl*	—
5741.79	2	1	5878.97	5	2	6120.09	8*Bl*	—
5743.384	3	1	5880.68	—	3*H*	6124.52	5*p*?	1
5743.847	3c	1c	5885.94	4	2	6128.68	7c	4c
5745.93	1h	—	5893.43	15c	8c	6142.53	7c	4
5746.90	—	20h	5894.61	3	2	6148.11	10c	5
5751.43	40	20	5898.54	1	1	6154.91	5*p*?	—
5753.06	—	30h	5900.59	200c	100c	6157.83	—	2h
5753.26	3	—	5903.80	20c	10c	6164.30	12	5
5754.44	4c	2c	5904.48	5	2	6175.01	—	2h
5758.11	4h	2h	5910.55	2h	2h	6183.24	—	8h
5759.00	2c	1h	5920.16	1h	1h	6204.75	6	3
5760.33	80	30	5924.27	2h	1	6213.06	8	4
5764.98	40	20	5927.40	10	10	6219.59	5h	3h
5771.06	10c	5c	5928.234	12c	4c	6221.93	20	6
5774.83	4	2	5934.15	15c	10c	6245.08	2h	2h
5776.07	30c	20c	5937.07	1	—	6249.68	1	2
5779.08	2	2	5938.62	2	1	6251.76	20c	10c
5779.78	2	1	5948.69	2h	1	6260.77	8c	4
5780.31	8	3	5949.90	4	2	6275.41	4	3
5782.67	1h	—	5957.69	15	6	6285.81	—	5h
5787.52	80	30	5964.56	1	—	6286.38	6c	3c
5789.78	7c	3	5965.36	4c	2c	6309.24	4c	2h
5790.63	2h	2	5970.67	—	6h	6312.16	5c	1h

TABLE 2.—*Arc and spark spectra of columbium* ($Z=41$)—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
6325.78	4	2	6951.15	10*Bl*	4	7583.21	6	1
6331.51	1	1*h*	6966.89	10c	4c	7584.06	2	—
6334.10	3*h*	1	6971.61	10	4	7585.28	5*h*	1*h*
6346.24	4	2	6972.49	20	6	7603.40	5c	
6348.98	6	3	6975.05	8	3	7639.81	2	
6355.56	2c	1	6978.39	6	2	7647.64	4	
6375.95	2*p*?	1	6986.09	20	6	7659.02	2	
6422.06	4*p*?	—	6989.38	5	2	7703.33	6	
6423.76	2*p*?	—	6990.32	100	30	7726.68	60c	
6430.46	80c	20c	6996.11	10c	5c	7757.31	20	
6433.22	30	6	7014.90	5	2	7772.11	5*h*	
6449.83	5c	2	7023.48	30	10	7787.11	3	
6453.11	—	5*H*	7026.15	2	10	7862.68	3*h*	
6464.32	5*d*	4	7035.63	3+*p*	1	7868.58	4*h*	
6473.95	20*Bl*	1	7038.04	10	3	7873.41	25c	
6484.36	30*Bl*	—	7046.81	200	80	7885.31	60	
6494.94	8*Bl*?	—	7051.20	8c	3c	7926.40	1	
6497.84	8	2	7066.41	6	2	7938.89	30	
6544.61	80c	20c	7075.23	7	2	7952.25	20*Bl*	
6551.61	5*p*?	1	7091.27	5	2	7954.76	10	
6556.92	4	2	7098.94	50c	20c	7997.80	15*Bl*	
6574.73	8	3	7102.01	30c	10c	8017.23	5*h*	
6575.9	20*Bl*	3	7119.31	10	4	8045.17	6*B*?	
6591.60	40c+*B*	20c	7122.95	6	3	8118.17	7c	
6606.14	10	5	7126.17	30	10	8118.67	6*h*	
6607.30	10	5	7130.06	10	3	8135.20	80	
6614.15	20	10	7136.09	5*B*?	2	8173.03	6	
6616.68	4	2	7159.43	100	30	8176.23	3	
6626.97	4	2	7165.82	5c	1	8181.70	1	
6629.11	1	20*h*	7178.27	8c	2	8189.40	3*h*	
6660.84	300c	150c	7180.01	6	2	8190.66	3	
6677.33	200c	100c	7186.14	3	1	8211.23	3*h*	
6681.33	5+*p*	2	7191.37	10	3	8226.08	3*h*	
6689.24	3	1	7208.94	15c	4	8228.98	3*h*	
6696.44	5	5	7235.68	3*p*?	1	8240.00	50c	
6699.82	3+*p*	2	7241.80	5*h*	1	8262.41	3*h*	
6701.20	100	30	7252.35	40	8	8283.6	5*Bl*	
6703.18	5+*p*	2	7256.18	5	1	8320.93	500c	
6709.88	10c	3c	7258.90	7c	2	8346.08	60	
6717.55	7+*p*	3c	7262.78	2	—	8350.04	10*h*	
6721.96	8	3	7268.90	5c	1	8371.39	4*h*	
6723.62	150c	50	7274.77	6	2	8373.76	1*p*?	
6726.28	10+*p*	3	7276.76	4	1	8387.88	4*h*	
6728.83	3+*p*	2	7311.93	5c	2c	8389.36	3*h*	
6737.16	5*Bl*	2*Bl*	7317.03	10	3	8406.23	15c	
6739.88	80	30	7323.92	15.	2	8414.74	3	
6745.43	4+*p*	3	7328.38	20c	5	8417.08	4	
6769.79	6+*p*	3	7332.30	4	1	8433.90	4*h*	
6795.26	15+*p*	8	7340.25	2	—	8434.31	3*h*	
6828.11	150	50	7353.16	50c	15c	8439.77	25c	
6849.33	25c+*p*	10	7382.50	150c	50c	8453.47	2	
6857.14	3	2	7409.78	2	—	8475.98	150c	
6870.92	20	7	7419.83	4	1	8526.99	50	
6876.36	60	25	7428.50	4	1	8547.25	20c	
6879.90	10c	3c	7435.38	3	1	8560.54	30c	
6886.33	30c	10c	7436.02	4	1	8575.87	30c	
6888.48	10c	3	7452.88	4	1	8614.45	20c	
6902.89	50c	20c	7456.32	4	1	8681.94	2*h*	
6906.59	6	3	7459.07	2	—	8691.45	2*h*	
6908.07	40	10	7478.20	10	3	8695.10	2	
6918.32	60	20	7515.93	40	10	8697.55	40c	
6920.85	—	2	7519.77	20c	4	8717.09	4	
6929.05	—	4	7532.11	3	1	8740.96	20	
6940.90	7	30	7547.71	3c	1	8767.97	12	
6946.07	10	4	7574.58	100c	20	8769.57	7c	

TABLE 2.—*Arc and spark spectra of columbium (Z=41)*—Continued

λ_{air}A	Intensity and character		λ_{air}A	Intensity and character		λ_{air}A	Intensity and character	
	Arc	Spark		Arc	Spark		Arc	Spark
8782.55	2		9412.39	4		10109.92	4	
8798.22	3		9415.14	2*p*?		10156.57	3	
8799.76	7		9427.45	2*p*?		10181.33	10*c*	
8815.56	100*c*		9435.48	8*c*		10203.44	8*c*	
8896.4	5		9437.52	2*p*?		10229.04	2*p*?	
8897.5	6		9438.7	8*h*		10249.56	5*c*	
8905.78	30		9470.93	6		10272.30	2*p*?	
8913.18	2		9472.02	4		10306.4	2*p*?	
8915.76	4*c*		9474.57	5		10419.54	10*c*	
8930.70	3		9483.38	2*p*?		10436.5	2	
8933.43	6		9518.30	3*p*?		10448.37	3	
8959.75	20*c*		9549.13	8*c*		10452.53	3	
8967.76	20*c*		9568.30	2*p*?		10460.87	3	
8983.15	4		9595.06	60*c*		10496.22	5*c*	
9011.74	7		9598.72	6*c*		10522.7	3	
9039.18	8		9614.72	2		10525.50	5*c*	
9041.27	2*B*?		9620.96	10		10533.72	4	
9042.23	5*B*?		9626.88	100*c*		10563.7	10*c*	
9054.88	2		9631.11	50*c*		10588.70	7	
9061.43	20*c*		9650.97	12		10636.54	4	
9066.54	4*c*		9667.22	2*p*?		10663.3	2	
9084.91	7		9669.8	3		10706.8	3	
9117.68	7		9676.75	50		10863.2	5	
9123.60	3		9677.5	4		10872.6	3	
9125.25	10		9790.64	2*p*?		10907.9	5*c*	
9129.44	10*c*		9798.66	3*p*?		10917.0	2	
9131.6	4*p*?		9815.56	2*p*?		10920.7	5*c*	
9141.31	50*c*		9890.09	4*c*		10994.4	2*p*?	
9186.96	20		9896.6	5		10999.9	3*p*?	
9197.60	15		9910.35	20		11046.1	3*p*?	
9213.8	3*p*?		9912.26	25		11051.0	2*p*?	
9240.9	10*c*		9943.64	2*p*?		11075.7	1*p*?	
9299.2	10+*p*		9957.29	15		11079.7	3*p*?	
9323.54	40*c*		9965.44	4*c*		11134.8	3	
9341.52	3*p*?		9991.33	1		11149.6	3	
9344.4	4		10003.85	30*c*		11262.2	6	
9353.17	10		10019.40	2		11454.4	2	
9359.32	3*p*?		10042.54	10*c*				
9393.56	4		10067.4	20*cd*?				
9408.60	20		10084.46	5*c*				

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RESEARCH PAPER RP882

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ROUTINE DETERMINATION OF BORON IN GLASS

By Francis W. Glaze and A. N. Finn

ABSTRACT

A method for the routine determination of boric oxide in glass, based on the "partition" of boric acid between water and ether in the presence of hydrochloric acid and ethanol, has been developed. A slightly acid solution of the fusion of the glass is shaken with ether and ethanol, and the boric acid in the ether layer titrated. The partition coefficient is 0.403 at 25 ± 2° C. The advantages of this method are its speed and simplicity without material sacrifice of accuracy.

Boric oxide between 0.7 and 16 percent can be rapidly and accurately determined. Lime, magnesia, alumina, soda, iron, and arsenic, in amounts likely to be found in glass, do not interfere. Barium, fluorine, and abnormally large amounts of iron interfere slightly. Zinc interferes seriously.

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I. INTRODUCTION

The methods now used for the determination of boric oxide in glass, silicate minerals, and similar materials are of two general types: those requiring distillation of the boron and those not requiring it. Examples of the former are the Gooch [1],[1] and the Chapin [2] methods; of the latter, the Wherry [3], with its various modifications, and the Mylius [8] methods.

For occasional determinations of boric oxide, the distillation methods are cumbersome because they require a rather elaborate "setup" and a large supply of special reagents. The nondistillation methods can be handled more easily, but the necessary filtrations are time-consuming and the results are probably not as accurate as those obtained by distillation.

Since the determination of boric oxide in commercial glasses has become increasingly necessary in recent years, because of the more frequent use of borax or boric acid in making such glasses, a rapid,

[1] Numbers in brackets refer to references at the end of this paper.

simple, and reasonably accurate method is desirable. In connection with a study of experimental glasses at the National Bureau of Standards, a method possessing these advantages has been developed. It is especially useful if many determinations of boron are to be made on glasses of the same type. It is based on the relative solubility of boric oxide in water and an ether-ethanol mixture and involves a special application of Henry's law—the so-called "partition law." Ether alone proved unsatisfactory because it extracted only traces of boric oxide from the aqueous solution.

II. EXPERIMENTAL STUDY

As boric oxide is reasonably soluble in alcohols, it was decided to use mixtures of absolute ethanol and ether inasmuch as Herz and Kurzer [4] have shown that the partition law applies in the case of mixed solvents. To determine the most effective mixture of ethanol and ether, a series of solutions of boric acid in ethanol-water mixtures was prepared, each solution containing approximately 0.05 g of boric oxide and 1 ml of hydrochloric acid (sp gr 1.18) in 50 ml. One solution contained 5 ml of absolute ethanol in 50 ml of solution, the others 10, 15, 20, 25, and 30 ml, respectively. To each of these solutions in a calibrated 100-ml glass-stoppered graduate were added 50 ml of ether. The liquids were thoroughly mixed by vigorous shaking and allowed to stand until the ether and water layers had separated. The volumes of the layers were read to the nearest 0.1 ml. The concentration of the boric oxide in the ether layer was determined as follows:

A 50-ml portion was pipetted into a 250-ml erlenmeyer flask, two drops of *p*-nitrophenol added and the solution titrated to the *p*-nitrophenol endpoint with 0.5*N* sodium hydroxide. One ml of phenolphthalein was added and the titration continued to the phenolphthalein endpoint. A volume of 0.5*N* sodium hydroxide equal to three times that used between the two endpoints was added and the flask vigorously shaken. Its sides were washed down with distilled water and the volume of the aqueous layer was made up to 40 to 50 ml. The ether and ethanol were quickly removed by first heating on the steam bath and finally by boiling over a free flame. The volume was adjusted to 35 to 45 ml with distilled water, the solution allowed to cool, and then made just acid with 0.5*N* hydrochloric acid to *p*-nitrophenol. After warming on the steam bath, the carbon dioxide was removed by boiling under reduced pressure until cool. The solution was then titrated to the *p*-nitrophenol endpoint with 0.1*N* barium hydroxide, mannitol added, and the boric oxide titrated.

The amount of boric oxide in the total ether layer was calculated from the amount of boric oxide found in the 50-ml aliquot portion and the boric oxide in the water layer was obtained by difference. From the concentration of boric oxide in each layer, the "partition coefficient" $\left(K=\frac{C_{Et_2O}}{C_{H_2O}}\right)$ was calculated. The values of K for the mixtures containing 5, 10, 15, 20, and 25 ml of ethanol were 0.044, 0.100, 0.189, 0.263, and 0.440, respectively. The relation between these values and the volume, V, of ethanol added can be expressed by the empirical equation:

$$K=0.000637V^2_{EtOH}+0.032.$$

The addition of 30 ml of absolute ethanol produced complete miscibility. Hence, 25 ml of ethanol was used in the succeeding experiments as that volume gave the maximum value of K and could be conveniently measured by means of a standard pipette. The data in table 1 indicate that the partition coefficient is practically independent of the quantity of boric oxide present, and boric oxide is, therefore, in the same state of association in each of the layers.

The effect of shaking was studied in a series of experiments using a sample containing about 0.05 g of boric oxide. The solutions were shaken by hand three times a minute and about five seconds each time. As the values of K were practically constant for shaking periods ranging from 5 to 30 minutes, it was concluded that, for these clear solutions, equilibrium is reached in less than five minutes. In this series of experiments it was found that the substitution of 95 percent for absolute ethanol caused a decrease in the average value of K from 0.444 to 0.374.

TABLE 1.—*Effect of the amount of* B_2O_3 *on* K

B_2O_3 sol.+1ml HCl (sp gr 1.18)+H_2O=25 ml.
25 ml C_2H_5OH (abs.) and 50 ml $(C_2H_5)_2O$ added.

[Determinations made at room temperature]

Quantities involved	Experiment number—				
	1	2	3	4	5
B_2O_3 added, (g)	0.01099	0.03297	0.05495	0.08243	0.1099
$(B_2O_3)_{Et_2O}$, (g)	.00513	.01490	.02488	.03712	.04975
$(B_2O_3)_{H_2O}$, (g)	.00586	.01807	.03007	.04531	.06015
Et_2O layer, (ml)	62.4	62.6	63.1	63.2	63.1
H_2O layer, (ml)	35.2	34.1	34.0	33.7	33.8
$C_{Et_2O} \times 10^4$, (g/ml)	0.822	2.380	3.943	5.873	7.884
$C_{H_2O} \times 10^4$, (g/ml)	1.665	5.299	8.844	13.45	17.80
$K'=C_{Et_2O}/C_{H_2O}$	.494	.449	.446	.437	.443

Average K = 0.444.[a]

[a] The average in this and succeeding tables is adjusted and is obtained by means of the equation:

$$\text{Average } K=\frac{\Sigma\,(g\,B_2O_3 \times K')}{\Sigma\,(g\,B_2O_3)},$$

where K' is the value computed from the analytical data in each experiment.

The effect of variations in temperature, t, on the value of K was investigated, using a 20-minute shaking time and amounts of boric oxide varying from 0.14 to 0.73 g. At 1.5, 10, 21, and 30.5° C the values of K were 0.613, 0.520, 0.453, and 0.409, respectively. The variation of K with temperature is expressed by the equation, $K=0.668-0.0469\sqrt{t}$ (see curve 1, fig. 1).

1. EFFECT OF THE AMOUNT OF FLUX, SODIUM CARBONATE, USED IN DECOMPOSING THE SAMPLE ON THE PARTITION COEFFICIENT

Although 0.5-g samples of most glasses can be completely decomposed after fusion with 1 g of sodium carbonate, if intimately mixed beforehand, tests were made to determine the effect of varying the amount of flux by dissolving 1 g and 2 g of sodium carbonate, respectively, in varying amounts of a standardized aqueous solution of boric acid, and then determining the boric oxide in the ether layer as previously stated. Herz [5] states that sodium chloride decreases

the solubility of boric acid in water, and the sodium chloride equivalent to the amount of sodium carbonate used seems to have a greater effect in decreasing its solubility in the ether-ethanol layer. This can be seen by comparing the values of K in tables 1 and 2. These tables also show that sodium chloride decreases the volume of the water layer.

The effect of temperature variations on the value of K in the presence of sodium chloride was also studied. No work was done in

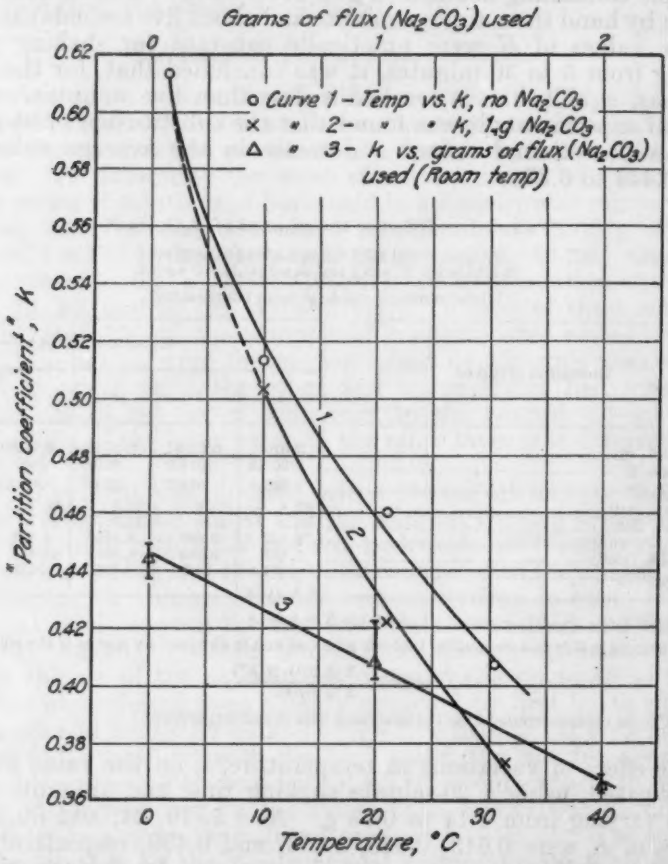

FIGURE 1.—*Effect of variations in temperature and in the amount of flux used in decomposing the sample on the "partition coefficient."*

the region of 0° C in this case after it was found that the value of K at 10° C fell off rapidly for amounts of boric oxide in excess of about 0.05 g. This did not happen in the experiments carried out at 21° C, so it would seem that there would be no advantage in using a temperature much lower than 20° C for the extractions. At the temperatures of 10, 21, and 31.5° C, K was found to be 0.503, 0.422, and 0.373, respectively, and the variation of K with temperature is expressed by the equation $K=0.673-0.054\sqrt{t}$. In figure 1 the effects of changes in temperature (curve 2) and the amount of flux (sodium carbonate) used on K (curve 3) are graphically shown.

TABLE 2.—*Effect of* NaCl *on K*

[Determinations at room temperature]

Quantities involved	Experiment number						
	6	7	8	9	10	11	12
Na_2CO_3 added, (g)	1.000	1.000	1.000	1.000	1.000	2.000	2.000
B_2O_3 added, (g)	.01075	.02150	.03225	.04300	.05375	.10000	.20000
$(B_2O_3)_{Et_2O}$, (g)	.00567	.01144	.01698	.02234	.02798	.05387	.10774
$(B_2O_3)_{H_2O}$, (g)	.00508	.01006	.01527	.02066	.02577	.04613	.09226
Et_2O layer, (ml)	71.9	71.6	71.6	71.5	71.6	74.0	74.3
H_2O layer, (ml)	26.3	26.6	26.6	26.6	26.6	23.4	23.1
$C_{Et_2O} \times 10^4$, (g/ml)	.789	1.598	2.372	3.124	3.908	7.280	14.50
$C_{H_2O} \times 10^4$, (g/ml)	1.932	3.782	5.741	7.767	9.688	19.71	39.94
K'	.408	.422	.413	.402	.403	.369	.363

Average $K = 0.408$ (1 g of Na_2CO_3).

Average $K = 0.365$ (2 g of Na_2CO_3).

2. EXPERIMENTAL WORK ON GLASSES AND INTERFERING ELEMENTS

One-half g samples of NBS Standard Sample 80,[2] which contains no boron, were fused in a platinum crucible with 1 g of sodium carbonate, cooled, digested in the crucible with varying amounts of a standardized aqueous solution of boric acid, and neutralized with hydrochloric acid (1:1) to the *p*-nitrophenol endpoint. The boric oxide in the resulting mixture (which contained some precipitated silica) was determined as previously outlined. The results obtained show that K is constant up to about 0.08 g of boric oxide; above that amount it is definitely low. Consequently, amounts of boric oxide up to 16.00 percent can be conveniently determined by this method. Since the value of K obtained in these experiments (0.408) is the same as that obtained when 1 g of sodium carbonate was used (table 2), silica, lime, magnesia, and soda do not interfere when present in amounts equivalent to those in Standard Sample 80.

TABLE 3.—*Partial composition of standard samples*

Constituents	NBS Standard Samples—			
	80	93	91	92
	%	%	%	%
SiO_2	74.10	80.600	67.60	----------
R_2O_3	.42	2.060	6.00	----------
CaO	4.65	----------	10.48	----------
MgO	3.23	.027	.01	----------
Na_2O	16.65	4.160	8.46	----------
K_2O	.04	.16	3.24	----------
B_2O_3	None	12.76	None	0.70
	Ignition loss=0.30	----------	F=5.75	----------

Since commercial glasses may contain appreciable amounts of arsenic, aluminum, barium, zinc, iron, and fluorine, tests were made to determine if these elements interfere. The tests were made by

[2] The partial composition of Standard Sample 80 of the National Bureau of Standards and of the other standard samples used in this work is given in table 3.

adding appropriate soluble salts, in varying amounts, to fusions of several standard samples of glass, and determining the boron.

Arsenious and arsenic oxides were added in amounts between 0.002 and 0.025 g. Arsenious oxide up to 0.005 g and arsenic oxide up to 0.01 g caused no trouble; above these amounts a plus error resulted in the value of K.

Alumina up to 0.05 g had no effect.

One-hundredth g of barium oxide did not affect the determination of boric oxide in Standard Sample 92, but caused low results on Standard Sample 93. However, the interference of small amounts of barium oxide can be avoided by adding a drop of sulphuric acid (1:1) when decomposing the fusion.

The equivalent of 5 percent of zinc oxide added to Standard Sample 80 gave a titration indicating 3.5 percent of boric oxide. This and other work leads to the conclusions that in the presence of zinc this method cannot be used until it has been removed and also that zinc chloride may lower the partition coefficient.

Iron, in the amounts usually present in glass, gave no trouble; but when it was added in amounts equivalent to 1 percent of ferric oxide the color of the ferric chloride formed from it masked the *p*-nitrophenol endpoint.

The presence of approximately 6 percent of fluorine caused a blank about twice that of the normal blank (0.56 ml of barium hydroxide solution as against 0.27 ml). Furthermore, low values of the partition coefficient were obtained, probably on account of the formation of potassium fluoborate (or possibly sodium fluoborate) which, according to Smith, Hamilton, and Graham [7], is quite insoluble under the conditions of the experiment.

It is evident from curve 2 of figure 1 that the effect of temperature on the partition coefficient cannot be disregarded. A constant-temperature room would insure very satisfactory conditions for making boron determinations by this method and, unless one is available, proper temperature corrections must be made if one wishes to obtain reasonable accuracy. However, for routine work ordinary variations in the temperature of the laboratory will not produce serious errors in the determination of small amounts of boric oxide (up to 8 percent) even if the temperature corrections are not applied. The error gradually increases for increasing amounts of boric oxide until, for 16 percent, it becomes about 0.2 percent (plus or minus, depending on whether the temperature is 2° below or above 25° C).

It can be seen from curve 3 of figure 1 that variations in the amount of flux used in decomposing the glass have a definite effect on K, but the effect is not as great as the temperature effect and is not serious, because a definite weight is much more easily obtained than a constant temperature.

III. RECOMMENDED METHOD OF ANALYSIS

1. REQUIRED REAGENTS

(1) *Para-nitrophenol.*—One gram dissolved in 75 ml of ethanol (95 percent) and made up to 100 ml with distilled water.

(2) *Phenolphthalein.*—One gram dissolved in 100 ml of ethanol (95 percent) and made up to 200 ml with distilled water.

(3) *Hydrochloric acid*, 0.5*N*.
(4) *Sodium hydroxide*, 0.5*N*.
(5) *Barium hydroxide*, 0.1*N*.
(6) *Ethanol, absolute.*
(7) *Ethyl ether, free from aldehyde and peroxide* (as indicated by test given below).
(8) *Mannitol.*

2. ANALYTICAL PROCEDURE

Grind 0.5 g of glass and 1 g of sodium carbonate intimately together in a mortar and transfer to a platinum crucible. Fuse at as low a temperature as possible and only as long as is necessary to effect complete decomposition. Cool, wash the lower surface of the lid, catching the washings in the crucible, and wash down the sides of the crucible with hot distilled water. Disintegrate the melt (with the aid of a platinum wire) on the steam bath and concentrate to about 5 ml. Cool and neutralize most of the alkali with HCl (1:1), guarding against loss of boron both by spattering and volatilization. Add two drops of *p*-nitrophenol, complete neutralization dropwise, add 1 ml of concentrated HCl (sp gr 1.18), and transfer to a calibrated, 100-ml glass-stoppered cylinder. Dilute to 25 ml, add 25 ml of absolute ethanol and 50 ml of ether[3] and shake intermittently for 20 minutes, noting the temperature. Allow the layers to separate, record their volumes, and pipette off a 50-ml sample of the ether layer for analysis. To the 50-ml sample, in a 250-ml erlenmeyer flask, add two drops of *p*-nitrophenol and titrate to the *p*-nitrophenol endpoint with 0.5*N* NaOH. Read the burette, add 1 ml of phenolphthalein, and continue the titration to the phenolphthalein endpoint. Add a volume of 0.5*N* NaOH equal to three times that used between the two endpoints, and shake the flask vigorously. Wash down the sides with distilled water and make the water volume up to 40 to 50 ml. Boil off the ether and ethanol as quickly as possible,[4] first on a water or steam bath and finally over the free flame to remove the last traces of ether and ethanol. Adjust the volume with distilled water to 35 to 45 ml, cool, and then make just acid with 0.5*N* HCl. Warm on the steam bath for about one minute and boil under reduced pressure until cool to remove CO_2. Titrate to the *p*-nitrophenol endpoint with 0.1*N* $Ba(OH)_2$, record the burette reading, add mannitol, and titrate the B_2O_3. 1 ml of 0.1*N* $Ba(OH)_2$ is equivalent to 0.00348 g of B_2O_3. A blank determination should be made using a glass, preferably of similar composition, but containing no boron.

[3] It became evident during the course of this work that the quality of the ether used in this method must be examined at frequent intervals and should be purified if the *p*-nitrophenol endpoint is not sharp or if the sample, after removal of the ether and ethanol and subsequent acidification, shows color. A satisfactory test method is to treat approximately 50 ml of ether, 5 ml of 0.5*N* NaOH, and about 50 ml of distilled water exactly as a sample would be treated for the removal of ether and ethanol. Upon diluting to 35 to 45 ml and neutralizing with 0.5*N* HCl to the *p*-nitrophenol endpoint, no color should be evident. For purification, a modification of the method of Palkin and Watkins [6] was used. The ether was first agitated with asbestos impregnated with alkaline permanganate (5 ml of saturated $KMnO_4$ to 15 ml of 33-percent NaOH) and then slowly siphoned, in a very fine stream, through a column of the alkaline permanganate into a bottle. This bottle also contained asbestos impregnated with alkaline permanganate and was kept in a cool, dark place.

[4] Long standing on the water or steam bath gives a colored acid solution which has a tendency to mask the *p*-nitrophenol endpoint in the final titration.

The equation for calculating the percentage of B_2O_3 in a 0.5-g sample, is as follows:

$$\text{Percent } B_2O_3 = 4(B_2O_3)_{50Et_2O}\left[V_{Et_2O} + \frac{V_{H_2O}}{K}\right],$$

where $(B_2O_3)_{50Et_2O}$ is the grams of B_2O_3 in the 50-ml aliquot portion taken for analysis, and V_{Et_2O} and V_{H_2O} the volumes of the ether layer and water layer, respectively. For routine work, where the temperature does not vary more than 2° from 25° C, 0.403 may be used as the value of K without significant sacrifice of accuracy; otherwise its value must be calculated from the equation, $K = 0.673 - 0.054\sqrt{t}$ (see table 4).

TABLE 4.—*Results obtained with samples containing varying amounts of* B_2O_3, *when proper temperature corrections are made*

NBS Standard Samples used	B_2O_3 present or added	Extraction temperature	Et_2O layer	H_2O layer	K[1] (calculated)	B_2O_3[2] present or added	B_2O_3 found	Difference
Number	g	°C	ml	ml		%	%	%
80	0.00480	21.5	72.3	25.8	0.423	0.96	1.05	+0.09
80	.00959	23.0	72.7	25.2	.414	1.92	2.00	+.08
80	.02467	24.0	72.6	25.4	.408	4.93	4.92	−.01
80	.04934	26.0	73.0	25.0	.398	9.87	9.96	+.09
80	.07401	26.0	72.8	25.3	.398	14.80	14.77	−.03
92	.00350	24.5	72.7	25.3	.406	.70	.78	+.08
80 and 93	.00629	19.0	72.1	25.5	.438	1.26	1.24	−.02
80 and 93	.01257	17.5	72.1	25.8	.447	2.52	2.59	+.07
80 and 93	.02515	18.0	72.7	25.5	.444	5.03	4.97	−.06
80 and 93	.03772	25.0	72.4	25.9	.403	7.54	7.67	+.13
80 and 93	.05030	25.0	72.5	25.7	.403	10.06	9.96	−.10
93	.06287	27.0	72.6	25.4	.393	12.57	12.58	+.01

[1] $K = 0.673 - 0.054\sqrt{t}$.
[2] On the assumption that the "boric oxide present or added" was in 0.5-g sample of glass.

The experimental work on this subject was started by J. F. Klekotka, and the authors acknowledge his assistance and thank him for the part of the work he did.

[3]

$$K = \frac{C_{Et_2O}}{C_{H_2O}} \text{ or } C_{H_2O} = \frac{C_{Et_2O}}{K}$$

$$C_{Et_2O} = \frac{(B_2O_3)_{50Et_2O}}{50} \text{ and } C_{H_2O} = \frac{(B_2O_3)_{50Et_2O}}{50\ K}$$

$$(B_2O_3)_{Et_2O} = C_{Et_2O} \times V_{Et_2O} = \frac{(B_2O_3)_{50Et_2O}}{50} \times V_{Et_2O}. \quad (1)$$

$$(B_2O_3)_{H_2O} = C_{H_2O} \times V_{H_2O} = \frac{(B_2O_3)_{50Et_2O}}{50K} \times V_{H_2O}. \quad (2)$$

$$\text{The total } B_2O_3 = (1)+(2) = \frac{(B_2O_3)_{50Et_2O}}{50}\left[V_{Et_2O} + \frac{V_{H_2O}}{K}\right]$$

$$\text{Percent } B_2O_3 = \frac{100 \times B_2O_3}{0.5} = 4(B_2O_3)_{50Et_2O}\left[V_{Et_2O} + \frac{V_{H_2O}}{K}\right]$$

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WASHINGTON, February 25, 1936.

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SOIL-CORROSION STUDIES, 1934. RATES OF LOSS OF WEIGHT AND PITTING OF FERROUS SPECIMENS

By K. H. Logan

ABSTRACT

The soil-corrosion investigation which was started in 1922 was originally planned to cover 12 years, plus the time required to write the final report. In 1934 the last of the original specimens were removed from 23 soils, but additions to the original test have so altered the plans that there now remain in the ground 7,500 specimens buried by the National Bureau of Standards and approximately 2,000 specimens of protective coatings prepared by research associates.

In general, the results of the examination of the specimens removed in 1934 confirm earlier conclusions. The additional data permit the calculation of the standard errors for certain classes of data.

The average maximum penetrations for the wrought-iron, Bessemer, and open-hearth specimens do not differ by more than a few percent. The specimens of open-hearth iron and of open-hearth steel containing 0.2 percent of copper appear to pit slightly more deeply than the other wrought specimens. In some soils cast iron corrodes somewhat more rapidly than steel.

Soils differ so greatly in corrosiveness that the average rates of corrosion or the average life of a pipe have little practical value.

The addition of chromium to steel reduces the loss of weight by corrosion and the number of pits, but even a large percentage of chromium will not prevent serious pitting. This is especially true with respect to soils containing chlorides. The addition of nickel, with or without chromium, tends to reduce the depth of the pits.

Certain materials seem to be especially suited or unsuited to certain types of soils.

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I. INTRODUCTION

In 1922 the National Bureau of Standards undertook to determine the corrosiveness of 46 soils selected for the most part by the U. S. Department of Agriculture as representative of the soils in various parts of the country which contained extensive installations of pipes. This determination was to be accomplished through the examination at 2-year intervals of 1 of 6 sets of the commonly used ferrous pipe

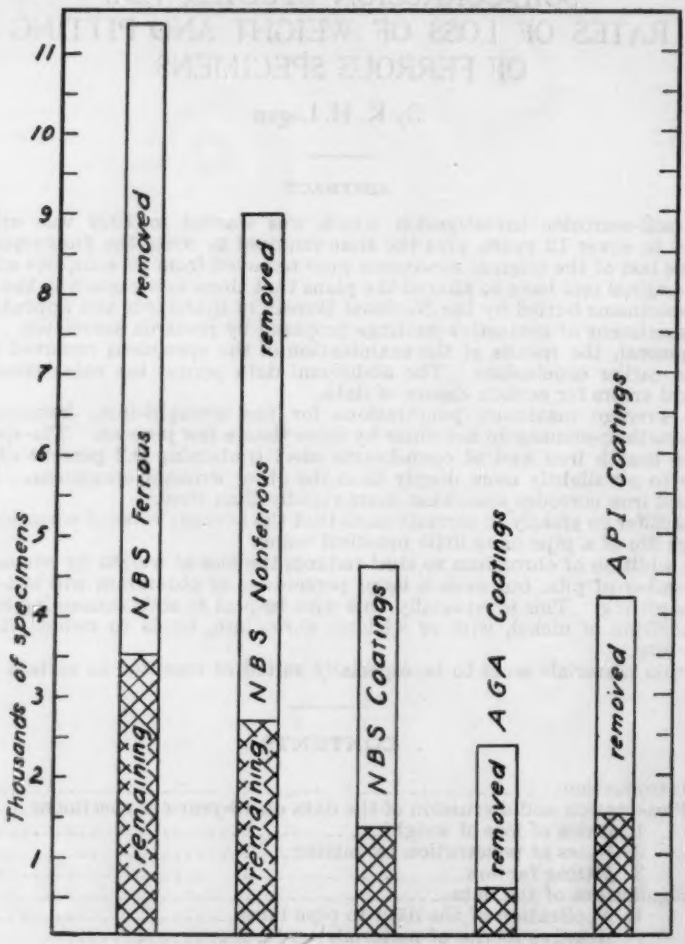

FIGURE 1.—*Status of the soil-corrosion investigation.*

materials. From time to time progress reports on this work have been issued. It was expected that at the close of the investigation all of the essential data and conclusions would be assembled in a single final report.

In 1934 the sixth and last set of the original specimens was removed from 23 soils, and this report presents the data on these specimens as well as on specimens from 39 other test sites. These sites include all the 12-year-old specimens. It is not advisable, however, to issue a final comprehensive report on the soil-corrosion investigation at this time because the investigation has been extended from time to

time by the burial of specimens of other materials and because specimens of the original materials have been left in the less corrosive soils. The status of the field investigation as of January 1, 1936, is shown in figure 1.

This report like previous ones on this investigation is a progress report, although an attempt is made to state more definitely the significance of that part of the investigation which has been completed. Since only 1934 data are tabulated, and only such parts of preceding papers are reproduced as are essential to the correlation of the 1934 data with earlier data, the reader must refer to some of the earlier reports for detailed information regarding the investigation. In Technologic Paper T368[1] the nature of the investigation, the soils, and the materials buried in 1922 and 1924 are described. In Research Papers 329,[2] 359,[3] and 638 [4] the data obtained up to 1932, inclusive, are summarized. A study of these papers is essential to a correct interpretation of the data presented in this report, since the results of any experiment depend largely on the conditions under which it is conducted.

Since the beginning of the soil-corrosion investigation in 1922 a considerable number of new varieties of pipe for underground use have been developed. These developments have been based largely on the behavior of the new materials when exposed to water or to the atmosphere, and at present there is no laboratory test which will indicate the resistance of a new material to soil action. Since few pipe makers have the facilities for testing their products underground, except through trial installations which do not provide an opportunity for comparing the results with the performance of more than one or two other materials, it seemed desirable that a series of field tests similar to the earlier tests should be arranged for the purpose of trying out the new materials under known conditions. It was hoped that a correlation of the characteristics of the materials with the results of the tests would furnish suggestions for further improvements. A test of some of these materials was therefore started in 1932, in which 10 specimens of each material were buried in each of 15 soils.

The soils, their locations, and the utilities cooperating in the 1932 tests are shown in table 1. The following manufacturers furnished one or more of the materials used.

Allegheny Steel Co.
American Brass Co.
American Machine and Foundry Co.
American Radiator Co.
American Sheet and Tin Plate Co.
Ball Chemical Co.
Bridgeport Brass Co.
Cast Iron Pipe Research Association.
Chadeloid Chemical Co.
Chase Brass and Copper Co.
Electro Metallurgical Co.
Ferro Enamel Corporation.
P. D. George Co.
Goodyear Tire and Rubber Co.
Harpoon Paint Products, Inc.
International Nickel Co.
Irvington Varnish and Insulator Co.
Johns-Manville Co.
McWane Cast Iron Pipe Co.
Mueller Brass Co.
National Tube Co.
Reading Iron Co.
Republic Steel Corporation.
Revere Copper and Brass Inc.
Ross-Meehan Foundries.
Scovill Manufacturing Co.
Sharon Steel Hoop Co.
Thiokol Corporation.
Walworth Alabama Co.

[1] K. H. Logan, S. P. Ewing, and C. D. Yeomans, *Bureau of Standards soil-corrosion studies: I. Soils, materials, and results of early observations.* Tech. Pap. BS 22, 447 (1928). T368, 50¢.

[2] K. H. Logan and V. A. Grodsky, *Soil-corrosion studies, 1930. Rates of corrosion and pitting of bare ferrous specimens.* BS J. Research 7, 1 (1931) RP329, 10¢.

[3] K. H. Logan, *Soil corrosion studies: Nonferrous metals and alloys, metallic coatings and specially prepared ferrous pipes removed in 1930.* BS J. Research 7, 585 (1931). RP359, 10¢.

[4] K. H. Logan and R. H. Taylor, *Soil-corrosion studies, 1932. Rates of loss of weight and pitting of ferrous and nonferrous specimens removed in 1932 and metallic protective coatings.* BS J. Research 12, 119 (1934) RP638, 5¢.

TABLE 1.—*Soils, test sites, and cooperating utilities in the 1932 tests*

Soil	Name of soil	Approximate location	Cooperator
51	Acadia clay	Spindletop, Tex	Sinclair-Prairie Pipe Line Co. of Texas.
52a	Alkali knoll	League City, Tex	Humble Pipe Line Co.
53	Cecil clay loam	Atlanta, Ga	Atlanta Water Department.
54a	Fairmount silt loam	Cincinnati, Ohio	Union Gas and Electric Co.
55	Hagerstown loam	Baltimore, Md	Baltimore Water Department.
56	Lake Charles clay	El Vista, Tex	Gulf Pipe Line Co.
57	Merced clay adobe	Tranquillity, Calif	Standard Oil Co. of California.
58	Muck	New Orleans, La	Sewerage and Water Board of New Orleans.
59b	Peat	Kalamazoo, Mich	Department of Public Utilities.
60	do	Plymouth, Ohio	Ohio Fuel Gas Co.
61	Sharkey clay	New Orleans, La	New Orleans Public Service Co.
62	Susquehanna clay	Meridian, Miss	Water Department.
63	Tidal marsh	Charleston, S. C	Do.
64	Salinas loamy sand	Cholame Flats, Calif	Union Oil Co.
65	Alkali soil	Wilmington, Calif	Shell Oil Co.
66	Mohave sandy loam	Phoenix, Ariz	Phoenix Water Department.
67	Cinders	Milwaukee, Wis	Milwaukee Gas Light Co.
68a	Gila clay	Phoenix, Ariz	Phoenix Water Department.
69a	Alkali soil	Wilmington, Calif	Shell Oil Co.

a Incomplete sets, mostly ferrous materials.
b No specimens removed in 1934.

In order to get some of the tables into compact form it has been necessary to refer to the materials by symbols. These are given in table 2. It will be noticed that more than one material has been assigned the same letter. To determine the significance of a letter it is, therefore, necessary to know the size or class of material involved.

TABLE 2.—*Identification of specimens*

1¼-INCH PIPE, 5 INCHES LONG

Identification letters	Material	Nominal thickness
		Inch
a	Open-hearth iron, lap-welded	0.145
b, d	Hand-puddled wrought iron, butt-welded	.145
e	Bessemer steel, butt-welded	.145
y	Treated Bessemer steel, scale-free, butt-welded	.145

3-INCH PIPE, 5 INCHES LONG

A	Open-hearth iron	0.216
B, D	Hand-puddled wrought iron	.216
K	Open-hearth steel	.216
M	Bessemer steel	.216
N	Bessemer steel, scale-free, butt-welded	.216
Y	Open-hearth steel, 0.2 percent of copper	.216

6-INCH CAST-IRON PIPE, 5 INCHES LONG

A	Southern cast iron	0.480
C	deLavaud centrifugal process	.450
CC	deLavaud centrifugal process, outside only exposed to soil	.450
I	Monocast centrifugal process	.450
L	Pit cast, northern ore	.480
MC	Pit cast iron, machined surfaces, (4 inches)	.250
MD	deLavaud cast iron, machined surfaces	.225
P	Pit-cast iron, southern ore	.480
Z	Pit-cast iron, southern ore, rough surfaces	.450

TABLE 2.—*Identification of specimens*—Continued

MISCELLANEOUS FERROUS CASTINGS

Identification letters	Material	Nominal thickness
		Inch
E	Cast-steel elbow, 2-inch	
S	Malleable-iron elbow, 2-inch	
V	High-tensile cast-iron nipple, 2½-inch O. D	0.5
None	High silicon cast-iron, 3 by 6 inch	.310

MISCELLANEOUS WROUGHT MATERIALS

C	26% Cr alloy pipe, 1 by 6 inch	9.250
C'	1.5% Cu steel pipe, 2 by 17 inch	.185
D	Wrought-iron pipe, ground surface, 2 by 17 inch	.185
K	Wrought-iron pipe, mill-scale surface, 2 by 17 inch	.185
M	Bessemer steel pipe, ground surface, 2 by 17 inch	.140
P	Bessemer steel pipe, mill-scale surface, 2 by 17 inch	.185

FERROUS MATERIALS BURIED IN 1932 (1½ by 12 inches long, except as noted)

[See table 16 for analyses of materials]

A	Puddled wrought-iron pipe	0.145
B	Puddled wrought-iron pipe	.145
D	Cu-Ni steel pipe	.145
E	High alloy cast pipe	.250
F	Sand-coated pipe, horizontally cast in green-sand	.250
G	Rattled pipe, horizontally cast in green-sand	.250
H	Cu-Mo open-hearth iron pipe	.145
I	Low alloy cast pipe, process A	.350
J	Low alloy cast pipe, process B	.350
K	KA2 sheet, 3 by 11 inches	.025
N	Low carbon tube, 2 by 10 inches	.154
P	5% Cr steel tube, 2 by 10 inches	.154
R	18% Cr, 8% Ni alloy tube	.145
S	17% Mn alloy sheet, 6 by 10 inches	±.063
T	17% Mn alloy sheet, 6 by 10 inches	±.063
U	12% Cr alloy sheet, 4 by 6 inches	±.063
V	17% Cr alloy sheet, 4 by 6 inches	±.063
W	18% Cr, 8% Ni sheet, 4 by 6 inches	±.063
X	18% Cr alloy tube	.145
Y	22% Cr, 12% Ni alloy sheet, 4 by 6 inches	.063

¾-INCH BOLTS, 4 INCHES LONG, WITHOUT NUTS

A	Decarburized iron (malleable)	
B	Malleable iron	
C	High-strength malleable iron	
D	Steel	

¾-INCH STEEL BOLTS, 3-INCHES LONG, WITH NUTS

D	Bare	
F	Lead-coated	
G	Sherardized	

In order to get the data for all of the materials in one soil into compact form it has been necessary to refer to the soils by number rather than by name. The names of all the soils and their approximate locations are given in table 3. In using this table it should be remembered that that part of the name which indicates the texture of the soil refers to the texture of the first 6 to 8 inches, i. e., to the A horizon and not to the texture of the soil in which the pipes were placed.

It should also be remembered that usually several quite different soils are to be found within the boundaries of a city. For example, there is very little Susquehanna clay in Meridian, Miss., near which the test of Susquehanna clay is conducted. The rates of corrosion should not be associated with the cities named but only with soil types.

TABLE 3.—*Soils and locations*

Soil	Soil name	Location	Soil	Soil Name	Location
1	Allis silt loam	Cleveland, Ohio.	36	Ruston sandy loam	Meridian, Miss.
2	Bell clay	Dallas, Tex.	37	St. Johns fine sand	Jacksonville, Fla.
3	Cecil clay loam	Atlanta, Ga.	38	Sassafras gravelly sandy loam.	Camden, N. J.
4	Chester loam	Jenkintown, Pa.	39	Sassafras silt loam	Wilmington, Del.
5	Dublin clay adobe	Oakland, Calif.	40	Sharkey clay	New Orleans, La.
6	Everett gravelly sandy loam.	Seattle, Wash.	41	Summit silt loam	Kansas City, Mo.
*7	Fairmount silt loam	Cincinnati, Ohio.	42	Susquehanna clay	Meridian, Miss.
8	Fargo clay loam	Fargo, N. Dak.	43	Tidal marsh	Elizabeth, N. J.
9	Genesee silt loam	Sidney, Ohio.	44	Wabash silt loam	Omaha, Nebr.
10	Gloucester sandy loam	Middleboro, Mass.	45	Unidentified alkali soil	Casper, Wyo.
11	Hagerstown loam	Baltimore, Md.	46	Unidentified sandy loam.	Denver, Colo.
12	Hanford fine sandy loam.	Los Angeles, Calif.	47	Unidentified silt loam	Salt Lake City, Utah.
13	Hanford very fine sandy loam.	Bakersfield, Calif.	51	Acadia clay	Spindletop, Tex.
14	Hempstead silt loam	St. Paul, Minn.	52	Alkali knoll	League City, Tex.
15	Houston black clay	San Antonio, Tex.	53	Cecil clay loam	Atlanta, Ga.
16	Kalmia fine sandy loam.	Mobile, Ala.	54	Fairmount silt loam	Cincinnati, Ohio.
17	Keyport loam	Alexandria, Va.	55	Hagerstown loam	Baltimore, Md.
18	Knox silt loam	Omaha, Nebr.	56	Lake Charles clay	El Vista, Tex.
19	Lindley silt loam	Des Moines, Iowa.	57	Merced clay adobe	Tranquillity, Calif.
20	Mahoning silt loam	Cleveland, Ohio.	58	Muck	New Orleans, La.
21	Marshall silt loam	Kansas City, Mo.	59	Peat	Kalamazoo, Mich.
22	Memphis silt loam	Memphis, Tenn.	60	Peat	Plymouth, Ohio.
23	Merced silt loam	Buttonwillow, Calif.	61	Sharkey clay	New Orleans, La.
24	Merrimac gravelly sandy loam.	Norwood, Mass.	62	Susquehanna clay	Meridian, Miss.
25	Miami clay loam	Milwaukee, Wis.	63	Tidal marsh	Charleston, S. C.
26	Miami silt loam	Springfield, Ohio.	64	Alkali soil	Cholame Flats, Calif.
27	Miller clay	Bunkie, La.	65	Alkali soil	Wilmington, Calif.
28	Montezuma clay adobe	San Diego, Calif.	66	Mohave sandy loam	Phoenix, Ariz.
29	Muck	New Orleans, La.	67	Cinders	Milwaukee, Wis.
30	Muscatine silt loam	Davenport, Iowa.	68	Gila clay	Phoenix, Ariz.
31	Norfolk sand	Jacksonville, Fla.	69	Alkali soil	Wilmington, Calif.
32	Ontario loam	Rochester, N. Y.	112	Imperial clay	Niland, Calif.
33	Peat	Milwaukee, Wis.	113	Imperial clay	Niland, Calif.
34	Penn silt loam	Norristown, Pa.	118	Niland gravelly sand	Niland, Calif.
35	Ramona loam	Los Angeles, Calif.			

* The correct classification of the soil at this location is in doubt.

II. PRESENTATION AND DISCUSSION OF THE DATA ON 12-YEAR-OLD SPECIMENS

1. RATES OF LOSS OF WEIGHT

The rates of loss of weight of the 12-year-old specimens, in ounces per square foot per year, are given in table 4. Rates of loss of weight furnish a fairly satisfactory basis for the comparison of materials exposed for the same period to the same soils and for the comparison of the corrosivities of different soils at the close of a given test period. For different periods of test the relative corrosivities of two soils may not be the same since in one soil the initial rate of loss may be maintained, while in another soil the rate may decrease because of the effect of the corrosion products or the settling of the soil in the trench.

TABLE 4.—*Average rates of loss of weight of 12-year-old specimens of ferrous pipe*[a]

[In ounces per square foot per year]

Soil	Duration of test	1¼-inch wrought specimens[b]				3-inch wrought specimens[b]				6-inch cast-iron specimens		
		a	b	e	y	B	K	M	Y	C	L	Z
	Years											
1	11.65	0.77	0.75	0.60	0.80	0.82	0.81	0.99	0.76	1.09	1.16	1.12
2	12.01	.50	.59	.48	.49	.53	.45	.55	.49	[c].64	.56	.42
3	12.10	.31	.41	.39	.43	.38	.34	.36	.38	[c].32	.33	.35
4	12.00	.59	.55	.56	.52	.59	.58	.58	.62	[c]1.90	.90	.84
5	12.10	.53	.63	.58	.45	.53	.60	.60	.59	[c]1.04	.70	.87
6	12.09	.08	.10	.12	.08	.09	.09	.13	.11	[c].08	.08	.10
7	11.52	.43	.45	.43	.37	.42	.43	.49	.49	.59	.49	.70
8	11.76	.71	.59	.65	.55	.74	.68	.71	.75	1.43	1.72	2.62
9	11.51	.41	.41	.45	.43	.42	.44	.40	.41	.59	.53	.57
10	11.95	.36	.46	.41	.36	.40	.37	.41	.43	.46	.48	.44
11	11.92	.14	.23	.17	.16	.17	.17	.15	.18	.14	.17	.19
12	12.10	.28	.37	.34	.32	.33	.30	.30	.27	[d]	.47	.37
14	11.76	.35	.39	.44	.39	.41	.36	.39	.40	.34	.42	.52
15	12.02	.67	.71	.64	.65	.69	.68	.68	.76	[c].82	.70	.67
16	12.00	.69	.69	.67	.61	.64	.63	.63	.63	[d]	.84	.76
17	11.78	.80	.73	.71	.77	.90	.87	.82	.85	.93	.78	.82
18	11.71	.25	.23	.26	.23	.17	.23	.21	.33	.23	.23	.41
19	11.63	.25	.30	.33	.29	.28	.30	.29	.30	.27	.47	.39
20	11.65	.57	.56	.52	.52	.48	.53	.52	.49	.53	.66	.88
22	11.65	.60	.66	.70	.61	.68	.59	.67	.60	.79	.71	[d]
23	12.09	1.67	1.75	1.64	1.69	1.71	1.62	1.64	2.01	2.32	3.27	[e]
24	11.95	.11	.11	.13	.12	.10	.12	.17	.10	.08	.06	.08
25	11.67	.29	.34	.30	.25	.24	.31	.28	.24	.31	.30	.28
26	11.52	.31	.37	.31	.30	.35	.32	.33	.30	.31	.39	.43
27	12.02	.59	.71	.73	.63	.69	.58	.68	.67	[c]1.07	.55	.68
28	9.60	1.63	1.61	1.71	1.75	1.75	1.69	1.62	1.84	[c].61	3.82	4.00
29	12.04	1.79	1.35	1.60	1.61	1.30	1.49	1.23	1.67	[c]5.28	2.86	1.73
30	11.62	.45	.48	.41	.46	.54	.50	.48	.45	.80	1.08	.85
31	12.04	.24	.25	.24	.22	.23	.23	.23	.29	[c].44	.19	.31
32	11.66	.27	.30	.28	.32	.31	.31	.36	.28	.36	.35	.55
33	11.67	1.21	1.20	1.23	1.22	1.23	1.00	1.10	1.20	1.36	1.39	1.70
34	12.00	.32	.40	.34	.26	.49	.36	.44	.40	.63	.58	.63
35	12.09	.14	.22	.18	.09	.15	.14	.21	.16	[c].26	.17	.54
36	12.04	.21	.27	.27	.24	.19	.23	.20	.20	[c].36	.16	.24
37	12.04	.69	.75	.64	.58	.69	.70	.75	.86	[c].20	.78	1.74
38	12.01	.18	.20	.23	.22	.20	.21	.19	.22	.18	.18	.18
39	12.00	.40	.46	.51	.43	.52	.45	.53	.42	.73	.77	1.19
40	12.04	.57	.66	.60	.56	.71	.71	.58	.70	[c]1.84	.95	1.13
41	11.99	.50	.51	.53	.45	.54	.53	.50	.50	.38	.45	.45
42	12.03	.88	1.42	1.04	.95	.74	.93	.92	1.11	[c].59	1.48	2.53
43	12.02	1.29	1.38	1.62	1.47	1.18	1.06	1.09	1.35	1.69	1.24	1.28
44	11.81	.25	.35	.41	.30	.30	.24	.29	.27	.32	.28	.34
45	11.73	.83	.77	.83	.79	.90	.96	.79	.95	1.07	[d]	1.28
46	12.00	.33	.42	.37	.37	.39	.36	.40	.40	.35	.46	.67
47	12.08	.19	.33	.25	.23	.27	.25	.23	.26	.34	.29	.35
Avg for all soils		.55	.59	.57	.55	.56	.55	.56	.59	[f].82	.78	.84

[a] See tables 2 and 3 for identification of specimens and soils.
[b] Includes wrought iron and steel.
[c] These specimens are approximately 10 years old. Only the outer surface was exposed to the soil.
[d] No specimens.
[e] Specimen destroyed; no weight-loss data.
[f] The average for the C specimens is not comparable with that for the other because of the shorter periods of exposure.

The same line of reasoning applies also to the rates of pitting, which will be presented in another section of this report. Because of this progressive change in the rates of loss of weight and the rates of penetration, the reader should take into account the data recorded in the reports previously referred to before attempting to estimate the life of a pipe material or the corrosiveness of a soil. It should be remem-

bered also that the recorded rates are for mechanically cleaned specimens and take no account of the value of the corrosion products as pipe materials, which value is known to be appreciable under some conditions. The conditions of the test under discussion do not permit a numerical expression of this value of corrosion products.

This may account for some of the cases in which the results of the test do not agree with reported field experience. The values given in table 4 are computed from the losses of 2 specimens of each material, except in the cases of the specimens L and Z. In most cases the losses of the two similar specimens agree quite closely, but occasionally they differ considerably, and in rare instances a specimen may show twice the loss shown by its mate. On this account small differences in the computed rates of loss have no real significance. It will be noted that in many of the soils the rates for the wrought materials (iron and steel) are nearly the same and somewhat smaller than for the cast materials. In different soils the rates differ widely.

From the standpoint of the service which a pipe is expected to render as a carrier of a fluid, the rates of loss of weight are, for most soils, unsatisfactory, since they take no account of the uneven distribution of the loss. Comparison of rates of loss of weight and rates of penetration for different soils will show that there is no close relation between the two, though, of course, pitting involves some loss of weight.

2. RATES OF PENETRATION BY PITTING

Table 5 shows the 12-year average maximum rates at which corrosion penetrated the pipe. The values are adjusted to make the rates for specimens of different sizes comparable. This adjustment has been discussed in Research Paper 329, page 8.

TABLE 5.—*Weighted average rates of maximum pitting of 12-year-old specimens of ferrous pipe* [a]

[In mils per year]

Soil	Duration of test	1½-inch wrought specimens [b]				3-inch wrought specimens [b]				6-inch cast-iron specimens		
		a	b	e	y	B	K	M	Y	C	L	Z
	Years											
1	11.65	7.9	6.2	7.1	5.8	6.3	7.8	8.2	10.3	9.9	10.5	13.2
2	12.01	4.7	4.0	4.6	6.7	4.5	4.3	3.8	4.8	• 4.2	4.8	7.3
3	12.10	7.4	6.6	5.1	4.5	5.3	5.0	5.7	6.4	• 4.5	9.9	12.1
4	12.00	12.5	6.5	6.5	6.8	6.2	8.6	5.9	12.2	•10.7	7.5	7.5
5	12.10	2.7	4.1	3.5	3.1	3.3	3.8	3.6	3.7	• 6.0	3.3	7.4
6	12.09	1.9	1.6	1.5	1.4	2.1	1.1	1.8	2.4	• 1.2	.8	.8
7	11.52	4.4	3.5	4.3	2.5	4.0	3.8	4.0	3.7	7.1	7.6	6.8
8	11.76	8.4	6.5	6.3	4.9	6.8	7.4	5.8	9.3	13.3	18.5	19.4
9	11.51	3.7	3.6	2.8	4.5	3.2	4.0	4.3	7.5	5.3	5.0	5.4
10	11.95	4.1	4.3	3.3	3.2	3.3	3.8	4.0	4.4	3.6	5.7	5.3
11	11.92	8.3	6.3	5.9	4.9	5.9	5.5	6.4	6.2	3.5	3.6	5.1
12	12.10	5.0	4.8	4.5	4.9	5.9	3.9	5.2	6.7	(d)	4.0	5.4
14	11.76	8.6	9.3	6.7	7.1	10.0	6.8	7.7	9.3	4.3	4.3	4.5
15	12.02	6.5	4.1	4.6	4.4	4.8	5.7	5.5	4.9	• 3.9	9.2	7.6
16	12.00	6.8	5.1	4.8	5.2	4.6	6.3	5.7	6.4	(d)	12.3	14.2
17	11.78	3.5	3.1	3.5	3.3	3.4	3.9	3.8	3.5	6.3	4.6	5.2
18	11.71	4.4	3.5	3.4	3.2	3.4	5.2	3.6	3.7	5.9	7.8	11.5
19	11.63	4.8	5.3	6.1	5.6	5.3	6.7	4.9	5.0	5.2	16.1	14.7
20	11.65	5.8	4.1	6.2	5.5	3.8	6.2	4.7	4.9	7.7	7.0	9.4
22	11.65	6.2	5.6	5.9	6.6	4.8	4.6	5.4	5.6	8.4	12.4	(d)

See footnotes at end of table.

TABLE 5.—*Weighted average rates of maximum pitting of 12-year-old specimens of ferrous pipe*[a]—Continued

Soil	Duration of test	1½-inch wrought specimens[b]				3-inch wrought specimens[b]				6-inch cast-iron specimens		
		a	b	e	y	B	K	M	Y	C	L	Z
	Years											
23	12.09	12.0	12.0	12.0	12.0	12.1	12.3	12.0	13.3	18.2	25.1	36.4
24	11.95	2.3	1.9	1.8	2.1	2.2	2.2	2.3	2.5	2.8	2.3	2.2
25	11.67	4.3	3.7	4.1	2.8	3.8	3.6	4.6	4.2	3.9	7.3	7.8
26	11.52	3.2	4.1	3.8	3.0	3.5	3.8	3.1	3.6	6.3	10.0	13.6
27	12.02	3.5	3.9	4.9	4.9	4.6	6.3	5.6	5.3	[c]9.0	9.2	9.2
28	9.60	15.1	13.8	14.3	15.1	16.7	18.8	14.8	22.3	[c]5.9	35.6	17.4
29	12.04	[c]16.2	7.4	11.3	12.0	9.3	16.1	8.4	14.2	[c]7.9	15.0	13.5
30	11.62	4.7	4.4	5.0	4.3	4.6	4.4	5.2	5.4	10.6	10.6	8.6
31	12.04	2.7	2.4	2.7	2.5	3.1	3.2	3.0	3.0	[c]3.8	1.5	5.2
32	11.66	4.9	3.7	3.9	4.3	5.0	7.0	5.0	7.7	5.8	8.0	10.3
33	11.67	9.6	8.3	7.7	8.9	8.5	8.4	7.7	6.8	9.0	13.7	15.4
34	12.00	4.8	3.0	3.4	2.7	4.2	2.9	3.7	4.6	7.5	5.5	4.1
35	12.09	.8	2.0	1.5	.4	2.6	1.6	4.7	1.9	[c]8.8	2.4	4.1
36	12.04	4.6	3.7	4.0	3.9	3.7	4.9	3.7	3.6	[c]4.3	4.1	3.3
37	12.04	6.3	5.3	6.5	5.6	6.1	5.0	7.6	10.0	[c]8.0	4.7	8.6
38	12.01	2.9	2.7	2.2	2.5	2.2	1.8	3.0	1.8	1.7	.8	.8
39	12.00	6.4	4.7	4.1	5.0	5.1	5.7	6.8	8.2	7.9	4.8	8.3
40	12.04	11.5	5.7	5.6	6.6	5.4	7.0	5.7	6.0	[c]6.5	5.7	7.5
41	11.99	8.4	7.8	6.6	7.6	6.7	5.9	6.1	6.4	3.4	4.7	5.0
42	12.03	7.6	7.3	9.2	7.1	6.7	10.3	7.2	8.8	[c]6.3	16.0	22.8
43	12.02	7.4	6.5	8.3	8.7	10.9	8.8	6.0	5.5	11.8	13.6	8.7
44	11.61	7.5	4.8	5.4	5.9	5.3	4.7	6.6	6.1	5.2	5.2	5.3
45	11.73	6.9	6.6	7.2	6.9	7.2	9.4	7.9	9.5	9.5	[d]	11.2
46	12.00	4.0	5.2	5.3	8.8	5.7	4.7	9.4	6.4	4.6	5.1	8.2
47	12.08	1.3	3.6	2.0	2.4	2.3	1.9	2.1	1.9	4.8	.9	2.2
Avg. for all soils		6.14	5.17	5.32	5.33	5.43	5.89	5.61	6.44	[f]6.6	8.38	9.27

[a] See tables 2 and 3 for identification of specimens and soils.
[b] Includes wrought iron and steel.
[c] These specimens are approximately 10 years old.
[d] No specimens.
[e] Punctured, 1932 data.
[f] The average for the C specimens is not comparable with that for the other specimens because of the shorter period of exposure.

The discussion of rates in the preceding section is equally applicable to the data in table 5.

Tables 4 and 5 are presented primarily to enable those who care to do so to interpret the results of the soil-corrosion data as they think best, and to enable them to confirm or contradict the conclusions which the author has drawn. They occupy a position midway between extensive and complicated tables of original observations on the one hand, and tables of computed data involving more or less questionable assumptions on the other. To be of use they must be interpreted. It will be noted that soils differ greatly in corrosiveness and that the relative resistance to corrosion of different materials is not the same for all soils.

3. PITTING FACTORS

Under some conditions the unevenness of a corroded surface is of interest. This unevenness is expressed mathematically by the pitting factor, which is the ratio of the depth of the deepest pit to the average thickness of the metal removed by corrosion. The value of this ratio is not a measure of the seriousness of corrosion since the ratio is 1, both for cases of no corrosion and complete destruction of the material tested. If corrosion were the result of segregations or impuri-

ties in the metal, the pitting factor would indicate, in a general way, the nonuniform character of the material. In underground corrosion, however, soil characteristics control both the extent and the distribution of the corrosion, and the pitting factor is affected by the character of the soil, and the duration of the exposure, as well as by the character of the material.

A comparison of the average values of the pitting factors in table 6 indicates that the corrosion of the wrought iron is slightly more uniform than that of the other materials, and that the distribution of the corrosion is less uniform on the larger specimens. However, the standard errors indicate the possibility that the differences in the average pitting factors are accidental except, perhaps, in the case of the open-hearth iron. The relation of soil characteristics to pitting factor has been discussed by Denison and Hobbs.[5]

TABLE 6.—*Pitting factor for 12-year-old specimens of ferrous pipe* [a]

[Ratio of the depth of the deepest pit to the average penetration as determined from loss of weight]

Soil	Duration of test	1½-inch wrought specimens [b]				3-inch wrought specimens [b]				6-inch cast-iron specimens		
		a	b	e	y	B	K	M	Y	C	L	Z
	Years											
1	11.65	6.91	5.20	7.39	4.84	5.20	6.59	5.71	9.15	5.87	6.64	13.56
2	12.01	6.20	4.32	6.18	8.98	5.65	6.52	4.86	7.39	4.42	5.40	10.89
3	12.10	16.28	10.76	8.86	7.00	10.69	10.68	10.86	12.04	11.09	20.18	24.75
4	12.00	14.15	7.67	7.73	8.64	7.85	10.18	7.89	13.29	38.85	5.19	6.00
5	12.10	3.36	4.27	4.02	4.42	4.36	4.23	4.02	4.48	8.36	3.18	6.17
6	12.09	15.44	10.66	8.65	12.78	16.77	9.42	10.79	16.78	16.51	6.21	5.05
7	11.52	6.83	4.98	6.65	4.40	6.25	5.85	5.37	5.62	7.56	15.44	5.65
8	11.76	7.86	6.82	6.36	5.88	6.68	7.51	8.74	9.38	6.26	6.96	4.55
9	11.51	5.98	5.58	4.07	6.74	5.18	6.25	6.99	13.47	5.51	7.10	6.44
10	11.95	7.50	6.07	5.28	5.77	5.98	7.52	7.05	8.35	5.19	7.66	8.78
11	11.92	38.68	17.48	22.41	20.11	27.11	23.35	30.09	26.43	17.00	19.35	17.62
12	12.10	11.83	8.40	8.83	9.82	11.86	9.58	11.84	16.85	(c)	6.12	11.57
14	11.76	16.39	16.21	9.96	12.01	17.00	12.71	14.07	15.49	10.05	7.84	5.73
15	12.02	6.44	3.67	4.72	4.47	5.01	6.61	5.77	4.42	3.38	9.17	9.74
16	12.00	6.46	4.76	4.89	5.57	4.71	7.40	6.18	7.23	(c)	8.94	12.15
17	11.78	2.89	2.79	3.25	2.83	2.55	3.01	3.25	2.76	4.55	3.56	4.22
18	11.71	11.79	10.21	8.74	9.55	12.98	16.83	11.88	8.43	19.20	22.73	17.83
19	11.63	12.85	11.68	12.27	12.52	14.14	16.09	12.44	11.86	12.91	22.23	33.30
20	11.65	6.84	4.75	7.70	7.03	5.18	8.68	6.12	7.18	9.21	7.80	6.97
22	11.65	6.81	5.49	5.99	7.16	4.88	5.32	5.50	6.58	6.95	12.37	(c)
23	12.09	4.82	4.40	4.78	4.68	4.59	4.99	6.60	4.75	5.04	4.78	(d)
24	11.95	14.86	10.95	8.82	12.05	14.70	12.87	14.00	16.45	2.50	2.86	1.80
25	11.67	10.09	6.94	9.10	7.10	11.25	8.32	11.22	12.27	8.03	18.10	19.65
26	11.52	7.01	7.09	8.18	6.60	7.12	8.16	6.54	8.16	12.74	18.69	20.57
27	12.02	3.89	3.55	4.90	5.17	4.28	7.68	6.61	6.00	5.56	15.80	13.30
28	9.60	6.13	5.47	5.50	5.69	6.35	7.41	6.41	7.99	3.49	5.66	3.00
29	12.04	(c)	3.63	4.61	4.89	5.54	8.08	5.26	8.43	1.19	3.47	5.24
30	11.62	6.78	5.88	7.95	6.31	5.39	6.07	7.30	8.39	8.47	6.71	6.98
31	12.04	7.64	6.23	7.89	7.43	9.50	9.42	9.61	6.92	6.98	5.28	11.86
32	11.66	12.30	7.72	9.21	9.00	10.39	15.39	9.70	17.90	10.21	15.06	13.11
33	11.67	5.31	4.48	4.01	4.78	4.63	5.95	4.92	3.88	4.62	7.29	5.71
34	12.00	9.39	4.74	6.71	6.72	5.93	5.45	6.32	10.45	7.68	6.58	4.69
35	12.09	4.04	4.76	4.91	2.90	12.23	8.38	19.17	9.75	21.72	9.68	4.77
36	12.04	15.15	9.06	10.15	10.81	12.88	13.75	12.50	11.68	11.19	18.83	10.39
37	12.04	6.17	4.53	6.72	6.37	6.28	4.92	6.93	8.11	4.88	4.57	3.54

See footnotes at end of table

[5] I. A. Denison and R. B. Hobbs. The corrosion of ferrous metals in acid soils. BS J. Research 13, 125 (1934) RP 696.

TABLE 6.—*Pitting factor for 12-year-old specimens of ferrous pipe* [a]—Continued

[Ratio of the depth of the deepest pit to the average penetration as determined from loss of weight]

Soil	Duration of test	1½-inch wrought specimens [b]				3-inch wrought specimens [b]				6-inch cast-iron specimens		
		a	b	e	y	B	K	M	Y	C	L	Z
	Years											
38	12.01	10.96	8.77	6.00	7.64	7.73	5.58	13.14	6.47	8.75	2.67	2.67
39	12.00	11.11	6.58	5.41	7.61	7.03	8.41	9.60	13.54	7.03	3.80	5.14
40	12.04	13.35	5.44	6.27	7.99	5.16	6.97	7.29	5.97	2.20	3.81	4.46
41	11.99	11.19	9.81	8.43	11.11	8.61	7.52	8.34	8.77	6.33	6.81	7.22
42	12.03	5.92	3.85	5.78	5.11	6.38	7.34	6.00	5.77	6.71	7.59	6.01
43	12.02	3.96	3.12	3.34	4.28	6.12	6.48	3.67	2.98	4.90	9.47	5.79
44	11.61	19.79	9.05	8.83	13.02	12.12	13.73	15.87	15.30	11.35	11.67	10.19
45	11.73	5.58	5.56	5.67	5.78	5.27	6.50	7.37	7.24	6.49	(c)	8.30
46	12.00	8.01	7.78	9.41	15.50	10.56	9.38	16.42	11.10	9.70	7.08	7.42
47	12.08	4.81	7.45	5.71	6.90	6.76	5.25	6.43	5.47	10.43	2.88	4.53
Avg		9.54	6.86	7.16	7.68	8.37	8.63	9.04	9.58	8.86	9.16	9.24
Standard error		0.92	0.47	0.46	0.52	0.68	0.57	0.72	0.61	0.98	0.87	0.98

[a] See tables 2 and 3 for identification of specimens and soils.
[b] Includes wrought iron and steel.
[c] No specimens.
[d] Specimen destroyed; no weight loss data.
[e] Punctured, 1932 data.

III. SIGNIFICANCE OF THE DATA

1. APPLICATION OF THE DATA TO PIPE LINES

Having examined the data presented in the preceding pages the reader may inquire as to their applicability to the corrosion of underground pipe systems. In the beginning, it should be stated that the tests deal directly with rates of corrosion and only indirectly with pipe life. Nevertheless, when properly interpreted, the data should be of value in the estimation of the service to be expected from pipe materials under various soil conditions.

It was pointed out in an earlier section of this paper that, other things being equal, the observed value of the deepest pit will depend somewhat upon the size of the area from which the maximum pit is chosen. This question has been discussed at length by Scott.[6]

While there remains some doubt as to the amount by which the pit depths on the unit area used in this report (the area of 1½-inch pipe, 5 inches long) should be increased to equal the pit depths on a length of pipe line exposed to similar conditions, there can be no doubt that some increase is required. The question is being investigated.

It was pointed out in an earlier report on the soil-corrosion investigation [7] that, at least for the earlier periods of exposure, the rate of corrosion decreases with time. Scott [8] expressed this relation by means of a formula. The problem is too complex for full discussion in this paper. The relation between the average maximum pit depth

[6] G. N. Scott. *Adjustment of soil corrosion pit depth measurements for size of sample.* Proc. API 14, IV, November 1933, p. 204.
[7] K. H. Logan, S. P. Ewing, and C. D. Yeomans. *Bureau of Standards soil-corrosion studies.* Tech. Pap. BS 22, 447 (1928), T368.
[8] G. N. Scott. *A preliminary study of the rates of corrosion of iron in soils.* Proc. API 14, IV, November 1933, p. 212.

and the length of the exposure of steel specimens to certain soils is shown in figure 2. It will be noted that the shapes of the curves are different for different types of soil. The curves also show the importance of considering the kind of soil to which the pipe is exposed.

In the determination of the rates of penetration the Bureau of Standards specimens were cleaned before they were placed in the soil, and after the specimens were removed from the soil the corrosion products were removed. The data, therefore, represent rates of penetration of the pipe wall by corrosion and not necessarily the rate of decrease in the ability of the material to resist pressure without leaking.

It is probable that working lines are subjected to other influences in addition to those affecting the corrosion of the National Bureau of Standards specimens. Some of these influences may accelerate corrosion, while others may retard it. If these influences are of importance it is to be expected that the corrosion of working lines will be

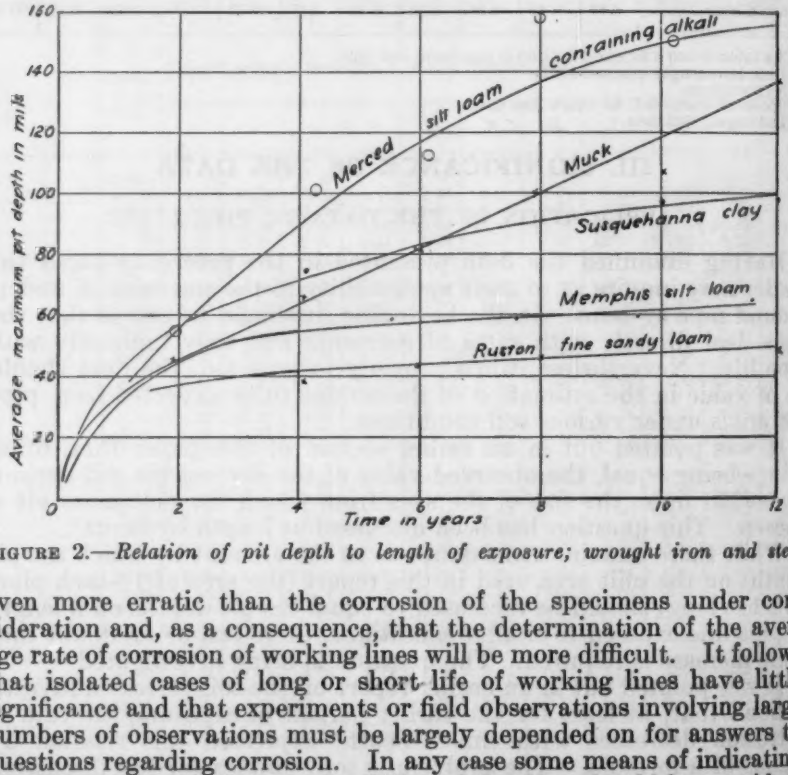

FIGURE 2.—*Relation of pit depth to length of exposure; wrought iron and steel*

even more erratic than the corrosion of the specimens under consideration and, as a consequence, that the determination of the average rate of corrosion of working lines will be more difficult. It follows that isolated cases of long or short life of working lines have little significance and that experiments or field observations involving large numbers of observations must be largely depended on for answers to questions regarding corrosion. In any case some means of indicating the dispersion and the reproducibility of the data should be provided.

Doubtless what has just been said regarding the relation of the soil-corrosion data to pipe-line corrosion leaves the reader uncertain as to how he can use the data. This is not because the data are not usable but because, as was said in the introduction to the report, the work is incomplete. So many facts regarding underground corrosion have been collected that it seems probable that a little additional work will yield positive answers to many corrosion problems.

2. RELATIVE MERITS OF MATERIALS

Although the purpose of the original soil-corrosion investigation was to determine the extent to which soils were responsible for corrosion underground, the question as to whether one material is more resistant to soil action than another is of such importance that the soil-corrosion data have been examined with respect to the relative corrosion-resistant properties of the materials tested.

A procedure has been adopted which involves a minimum of assumptions as to similarity of materials, areas, and rates of corrosion. The first step was to plot all of the pit depths for each material in each soil and to draw smooth curves for the data representing the trend of the data with respect to the duration of the exposure. If no specimens were missing, 12 points, 2 for each period of exposure, were plotted.

Points on this curve corresponding to the 6 periods of exposure were taken off, and the ratios of the last point to each of the others were computed. Then each plotted point or pit depth was multiplied by the ratio for the corresponding time of exposure, thus reducing all pit depths to corresponding pit depth for 12 years of exposure. The average pit depth, the standard deviation, and standard error were then computed for these 12 adjusted observations, i. e., for each material in each soil.

The magnitudes of the average pit depth and of the standard error depend of course on the way in which the curve referred to was drawn, and it is probable that in some cases at least more representative curves could have been drawn. This would have resulted in smaller standard errors and more accurate average values. Nevertheless, the worst result of an improperly drawn curve is an inaccurate average and a large standard error. The two taken together are true for any curve, although they may not be sufficiently precise to be of value. Since the purpose of the study was to determine whether or not the differences between the average rates of penetration could be accounted for by the dispersion of the data as indicated by the standard error, there was nothing to be gained by calculating the average rates of penetration for cases where the dispersion was obviously so great that a very large standard error would be obtained. In certain cases an average with a satisfactory standard error could be made by neglecting one or two points on the assumption that such points were the results of abnormal conditions with respect to soil or material. This, however, is a somewhat questionable procedure. Table 7 gives the average maximum pit depths for each material in each soil for which a satisfactory standard error could be computed by the method just outlined.

TABLE 7.—*Estimated average maximum pit depth at 12 years for each material*

1¼-INCH WROUGHT IRON AND STEEL (n=12)

Soil[a]	Open-hearth iron				Puddled iron				Bessemer steel				Treated Bessemer steel			
	δ[b]	$\overline{X}_0$	σ_m[c]	σ_s[c]	δ	$\overline{X}$	δ_m	σ_s	δ	$\overline{X}$	σ_m	σ_s	σ	$\overline{X}$	σ_m	σ_s
1	0	74.3	4.4	14.4	0	85.2	5.9	19.7	0	71.6	5.8	16.5	0	79.5	4.9	16.1
2	±3	63.0	6.8	19.3	±2	44.9	1.7	5.0	±3	54.4	2.6	7.4	±3	66.1	6.5	18.4
3	0	95.6	7.6	25.2	0	77.5	3.2	10.7	0	74.4	3.4	11.3	0	73.2	2.9	9.6
4	±2	137.3	18.7	56.0	{−1, ±2}	74.7	6.0	16.9	±2	71.0	4.5	13.4	±2	77.7	7.3	21.9
5	±3	38.4	3.3	9.4	±2	53.9	4.5	13.5	{+1, −1, ±2}	49.3	2.1	5.6	±2	38.3	1.6	4.9
6[f]																
7	±4	53.7	6.1	16.0	0	37.9	2.0	5.2	±4	42.9	3.5	9.4	±6	28.1	0.8	1.7
8	0	100.9	3.3	10.9	0	79.4	4.1	13.5	0	73.0	3.2	10.5	0	58.8	1.6	5.4
9[f]																
10	{−2, ±2}	50.4	3.8	10.2	±3	48.9	2.9	7.6	±2	35.2	3.8	11.4	±3	37.1	3.6	10.3
11	0	80.5	4.1	13.5	±1	74.1	3.6	11.3	0	75.1	2.9	9.8	0	69.6	4.0	13.4
12	±3	56.2	4.1	11.5	±3	53.4	7.5	21.2	±3	50.1	7.2	20.5	±4	58.3	5.1	13.5
13[f]																
14	0	109.9	8.0	26.5	0	111.5	7.8	25.7	0	143.0	12.7	42.1	0	140.3	9.0	29.8
15	±2	78.2	3.9	11.8	(f)	(f)	(f)	(f)	±2	61.9	3.7	11.0	±2	53.8	4.4	13.1
16	0	84.0	5.9	19.7	0	68.3	5.6	18.5	0	70.1	5.5	18.2	0	75.5	9.4	31.1
17	±4	41.0	1.3	3.4	±4	38.1	1.4	3.7	±4	41.8	1.4	3.6	±4	41.5	2.6	6.8
18	0	57.9	3.8	12.7	0	51.2	5.1	16.9	0	52.4	4.2	13.9	0	51.5	4.9	16.0
19	0	63.2	3.2	10.6	0	54.7	2.7	8.9	0	63.5	2.4	7.9	0	59.9	2.6	8.5
20	0	57.4	4.9	16.3	0	59.0	5.1	16.9	{+1, −1}	64.3	9.4	28.3	0	57.1	3.1	10.3
21[g]	±6	71.7	4.1	9.1	±6	48.2	2.8	6.1	±6	63.1	2.0	4.4	±6	66.4	4.9	11.0
22	0	65.0	3.8	12.7	0	64.2	1.4	4.8	0	66.2	1.8	5.8	0	67.4	3.0	10.1
23[h]																
24	±2	26.3	1.2	3.6	±2	21.2	1.0	2.9	±2	15.8	1.6	4.7	±2	23.1	1.8	5.3
25	±3	55.9	3.6	10.1	±3	46.7	2.5	7.1	±3	47.8	2.3	6.4	±2	38.1	1.9	5.8
26[f]																
27	±2	46.6	3.7	10.9	{+2, ±2}	49.2	2.4	6.4	±2	58.3	7.3	22.0	±2	48.5	4.5	13.5
28[i]	±4	174.4	9.6	25.3	±4	147.8	8.7	22.9	±4	155.2	6.6	26.0	±4	146.9	9.8	17.5
29	(i)	(i)	(i)	(i)	0	99.8	5.3	17.6	±1	117.7	8.0	25.4	0	121.5	5.7	18.9
30	±2	58.4	5.0	15.0	±3	50.2	1.2	3.3	±2	55.2	3.0	9.1	±2	55.5	3.9	11.6
31	±2	36.5	2.3	7.0	{+1, ±2}	33.9	2.9	8.1	{+2, ±2}	36.0	1.3	3.4	{+1, ±2}	40.8	5.3	15.0
32	0	63.2	5.7	18.7	0	50.5	3.4	11.3	0	50.2	3.3	11.0	0	49.5	2.3	7.5
33	±2	145.1	13.1	39.2	{+1, −1, ±2}	97.8	2.6	6.8	±2	80.9	7.4	22.2	±2	108.5	9.3	27.8
34[f]																
35[f]																
36	±2	57.0	2.2	6.6	±2	53.3	3.3	9.9	±2	45.7	2.0	6.1	±2	44.8	2.2	6.6
37	0	76.1	5.6	18.5	0	77.4	6.3	20.1	0	94.1	9.0	29.7	0	71.6	4.9	16.3
38[f]																
39	0	70.0	8.2	27.2	0	49.7	6.8	22.4	0	49.5	2.5	8.4	0	54.4	3.3	10.4
40	0	157.8	15.8	52.4	0	86.7	6.7	22.3	0	79.7	3.7	12.2	0	86.8	4.9	16.1
41	±2	106.8	5.3	15.9	±2	112.4	12.9	38.7	±2	81.0	4.0	12.0	±2	85.4	3.4	10.1
42	0	95.0	4.3	14.4	0	95.2	4.7	15.6	0	119.4	6.5	21.7	0	95.2	6.1	20.1
43	0	95.8	12.1	40.1	0	86.9	9.3	30.8	0	105.0	12.6	41.7	0	114.8	11.6	38.4
44	±2	87.7	7.6	22.7	±2	56.4	2.3	6.8	±2	66.3	2.0	6.1	±2	66.3	3.6	10.7
45	{+1, −1}	85.1	8.4	25.1	+3	51.0	3.3	10.6	+2	89.8	8.4	25.1	+2	78.5	3.4	10.2
46[f]																
47	±3	19.0	2.8	6.8	±2	27.0	3.9	11.6	±2	20.7	1.6	4.9	±2	19.8	3.0	8.9
Average[k]	----	83.6	2.4	37.3	----	69.1	2.2	34.2	----	75.0	2.2	34.1	----	72.4	2.1	32.4

See footnotes at end of table.

TABLE 7.—*Estimated average maximum pit depth at 12 years for each material*—Continued

3-INCH WROUGHT IRON AND STEEL ($n=12$)

Soil	Puddled iron				Open-hearth steel				Bessemer steel				Open-hearth steel +0.2% Cu			
	δ	$\overline{X}$	σ_m	σ_s	δ	$\overline{X}$	σ_m	σ_s	δ	$\overline{X}$	σ_m	σ_s	δ	$\overline{X}$	σ_m	σ_s
1	+2	75.9	1.9	5.6	0	96.7	4.9	16.3	±1	93.7	3.7	11.6	0	103.0	10.8	35.8
2	±2	56.6	3.2	9.7	±2	55.2	2.0	6.0	±3	53.8	2.2	6.1	±2	66.4	3.4	11.3
3	0	73.4	3.2	10.6	0	74.5	4.5	14.8	0	82.0	3.6	12.1	0	85.8	6.4	21.2
4	±3	89.4	4.0	11.2	±3	113.2	10.2	28.7	±2	90.0	11.2	33.7	+1, −2, ±2	157.3	17.2	42.1
5	±2	42.5	2.2	6.6	±2	68.7	6.3	18.9	±2	60.5	4.9	14.6	+1, −1, ±1	40.5	12.2	32.2
6 [f]																
7	±4	45.1	1.7	4.6	±4	44.7	3.2	8.6	±4	46.4	3.7	9.9	±4	38.3	3.3	8.8
8	0	77.0	5.2	17.4	0	96.0	5.1	16.8	0	100.0	5.2	17.3	0	130.2	9.2	30.5
9 [f]																
10	±2	45.4	3.9	11.5	±2	48.1	4.4	13.1	±2	62.7	8.6	25.7	±2	75.9	9.6	28.6
11	0	86.2	4.4	14.5	0	69.3	1.6	5.4	0	84.0	6.4	21.2	0	79.4	3.8	12.7
12	−2, ±3	81.1	6.8	16.6	−2, ±3	54.8	4.3	10.6	−1, ±3	70.1	2.6	6.4	−2, ±4	85.6	2.5	5.6
13 [f]																
14	±1	126.4	5.6	17.6	0	91.7	3.7	12.2	0	117.3	6.1	21.8	0	147.6	11.8	39.2
15	±2	63.4	6.2	18.7	±2	82.2	5.5	16.4	±2	68.5	4.5	13.6	±2	60.6	1.5	4.5
16	0	83.5	6.1	20.2	0	86.0	2.9	9.6	0	75.0	4.6	15.3	0	81.9	3.6	11.8
17	±4	44.3	0.8	2.2	±4	47.1	1.0	2.7	±4	48.8	2.8	7.3	±4	44.6	2.9	7.7
18	0	65.5	5.3	17.4	0	69.5	2.6	8.8	0	49.8	3.0	10.0	0	56.7	5.5	18.4
19	0	63.4	3.2	10.5	0	80.2	2.0	6.7	0	64.3	2.0	6.8	0	66.7	2.2	7.4
20	0	44.8	3.0	9.9	0	50.5	4.9	16.2	0	53.3	3.1	10.4	0	59.2	6.2	20.5
21	±6	60.3	7.5	16.8	±6	54.3	2.5	5.5	±6	64.0	3.3	7.4	±6	55.2	2.0	4.6
22	0	64.2	2.2	7.1	0	63.5	1.7	5.6	0	65.0	1.7	5.7	0	70.8	2.4	7.9
23	0	156.0	10.0	33.0	0	167.1	6.7	22.2	0	163.7	5.4	17.9	+3, −1, ±1	176.6	10.1	26.5
24	±2	24.8	2.8	8.4	±2	28.5	2.0	6.1	−2, ±2	30.5	1.9	4.9	±2	36.7	4.2	12.7
25	±2	51.7	3.0	8.8	±2	50.8	3.6	10.7	±2	57.6	2.9	8.7	±2	53.4	2.8	8.3
26 [f]																
27	±2	58.9	4.5	13.4	±2	83.5	5.1	15.2	±3	99.3	12.9	36.5	±2	76.3	4.6	13.7
28	±4	169.3	7.1	18.8	±4	207.5	11.1	29.1	±4	148.6	5.1	13.4	±4	221.1	8.9	23.6
29	0	126.4	6.9	22.9	0	216.1	10.1	33.3	0	142.6	13.1	43.4	(f)	(f)	(f)	(f)
30	±2	60.2	5.7	17.1	±2	64.7	7.9	23.6	±2	68.4	2.9	8.7	±2	61.3	5.1	15.2
31	±2	43.1	3.8	11.2	(f)	(f)	(f)	(f)	+2, ±2	40.1	2.5	6.5	+2, ±2	40.7	2.7	7.2
32	0	62.6	5.0	16.4	0	65.7	3.7	12.3	0	63.3	2.4	7.8	0	104.3	10.8	35.8
33	±2	131.3	14.0	42.1	±2	116.3	8.7	26.1	±2	114.5	18.9	56.6	±2	(f)	(f)	(f)
34 [f]																
35 [f]																
36	±2	48.0	1.2	3.5	±2	59.9	2.3	8.6	±2	51.9	1.4	4.1	±2	47.9	1.9	5.8
37	0	72.1	4.4	14.6	0	67.5	3.0	10.7	0	97.5	6.1	20.1	0	116.9	8.3	27.5
38 [f]																
39	0	64.2	4.1	13.7	0	74.4	8.9	29.6	0	69.3	4.4	14.7	0	100.0	4.3	14.2
40	0	70.2	3.2	10.6	0	105.4	7.9	26.3	0	82.6	5.4	17.7	0	82.5	4.5	14.8
41	±2	86.8	2.8	8.4	±2	73.6	3.9	11.7	±2	76.8	2.9	9.0	±2	78.7	6.0	18.0
42	0	92.2	25.6	84.8	0	124.6	3.9	13.0	0	108.2	4.0	13.2	0	115.6	4.1	13.5
43	0	138.4	6.6	21.8	0	130.7	9.6	31.9	0	102.7	9.1	30.0	0	101.5	13.1	43.4
44	±2	63.8	1.5	4.6	±2	62.0	3.5	10.6	±2	82.9	3.6	10.8	±2	89.4	4.0	11.9
45	+2	86.2	5.3	15.8	+2	111.3	5.8	17.3	+2	97.9	7.7	22.2	+3	80.5	2.2	6.9
46 [f]																
47	+1, ±2	31.8	3.3	9.5	+1, ±3	24.3	2.3	7.2	+1, ±2	23.6	1.1	3.2	±2	30.6	2.0	5.9
Avg. [k]	-----	76.8	2.0	31.1	-----	81.1	2.2	35.5	-----	78.7	1.5	23.9	-----	89.3	1.8	28.0

See footnotes at end of table.

TABLE 7.—*Estimated average maximum pit depth at 12 years for each material*—Continued

6-INCH CAST IRON

Soil	deLavaud ($n=12$)				Northern ($n=6$)				Southern ($n=6$)			
	δ	$\bar{x}$	σ_m	σ_s	δ	$\bar{x}$	σ_m	σ_s	δ	$\bar{x}$	σ_m	σ_s
1	0	147.1	9.7	32.3	+2	158.4	54.4	94.2	0	293.7	15.2	34.1
2	±7	51.1	3.0	5.9	±1	141.5	27.3	54.7	±1	92.2	3.8	7.6
3	+2, ±6	79.9	9.2	15.9	+1	295.5	34.8	69.5	0	176.5	2.7	5.6
4	±2	127.7	10.4	27.5	+1, ±1	60.0	60.6	5.9	−1, ±1	109.8	4.9	8.6
5	±6	73.0	3.5	7.9	±2	117.2	31.2	54.0	±2	111.4	5.9	10.2
6 [f]												
7	±4	63.4	6.0	14.8	−1, ±2	139.9	17.7	25.1	±3	80.7	22.1	31.2
8	±3	195.8	15.0	42.5	0	225.9	19.4	43.3	0	43.3	10.2	22.8
9 [f]												
10	+1, ±3	43.0	2.9	8.0	±1	106.9	23.9	47.8	±2	117.1	22.1	38.3
11	±2	84.0	24.1	72.3	±1	46.6	4.9	9.8	0	82.1	6.6	14.8
12	(f)	(f)	(f)	(f)	±1	41.3	4.6	9.2	−1, ±1	89.0	2.4	4.2
13 [f]												
14	0	70.3	8.3	27.7	0	69.2	7.2	16.0	0	69.2	8.9	20.0
15	±6	54.0	3.4	7.7	±1	137.9	14.2	28.3	+2, ±1	117.1	1.7	2.4
16	(f)	(f)	(f)	(f)	0	223.7	27.9	62.3	0	185.4	43.5	75.4
17	±4	95.1	7.6	20.2	±2	78.4	20.1	36.3	±2	71.4	10.9	18.9
18	−1, ±3	91.8	8.1	21.4	−1	124.9	6.6	13.2	−1, ±1	147.2	0.5	0.9
19	0	69.4	3.9	13.0	−1	205.8	5.1	10.0	0	295.3	32.3	72.2
20	−2, ±2	119.4	37.7	99.7	±1	107.9	25.4	50.9	±2	120.7	1.6	2.8
21	±6	52.3	3.2	7.0	±3	100.9	0.0	0.0	±3	57.0	0.0	0.0
22	0	111.2	5.4	18.0	0	162.3	16.3	36.5	0	178.2	8.6	19.2
23	0	246.9	13.8	45.7	0	339.9	20.9	46.8	0	448.7	34.0	76.0
24 [f]												
25	±3	45.7	3.9	11.1	±1	85.2	15.5	31.1	±1	143.9	38.2	76.4
26 [f]												
27	±6	102.7	8.2	18.3	±2	186.4	23.4	46.7	+1	202.7	12.7	22.0
28	±9	65.1	9.0	12.8	±2	383.9	67.0	115.9	(f)	(f)	(f)	(f)
29	(f)	(f)	(f)	(f)	±2	187.0	31.1	53.8	0	168.2	24.8	55.4
30	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	±2	116.7	9.3	16.1
31 [f]												
32	±1	84.1	8.3	26.2	0	136.1	24.7	55.2	0	244.0	85.0	190.0
33	±2	145.6	15.2	45.7	±1	219.1	29.3	58.5	±1	216.3	38.2	76.4
34 [f]												
35 [f]												
36	±6	72.0	5.5	12.2	+1, ±1	246.8	57.2	99.2	+1, ±1	376.1	71.4	123.6
37	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	+1, −1	115.7	4.6	6.2
38 [f]												
39	0	107.5	11.0	36.5	+1	52.6	2.4	4.7	±1	112.9	5.5	11.0
40	±6	67.0	3.9	8.9	0	89.9	9.7	21.8	0	110.2	7.8	17.5
41	−2, ±2	49.0	1.1	4.8	±1	68.7	10.7	21.4	±1	65.5	2.9	5.9
42	+1, −1, ±4	137.3	13.2	29.6	0	208.6	21.2	47.4	0	269.1	28.8	64.4
43	0	223.8	41.0	135.8	(f)	(f)	(f)	(f)	+1, −1	142.5	4.0	6.9
44	+1, −1, ±2	46.8	10.2	27.0	+1, ±1	65.7	3.7	6.5	±1	62.4	5.6	11.3
45	+4	87.8	6.0	15.9	+2	132.9	5.9	10.2	+1	186.0	5.8	11.7
46 [f]												
47	(f)	(f)	(f)	(f)	±1	20.9	2.1	4.2	±2	33.0	.4	.7

[a] See table 3 for identification of soils.
[b] δ denotes the number of specimens omitted in averaging because of unsatisfactory data. The sign of δ denotes whether the pitting of the omitted specimens was more or less than the average.
[c] $\bar{x}$ denotes the average maximum pit depth.
[d] σ_m denotes the standard error of $\bar{x}$.
[e] σ_s denotes the standard deviation.
[f] Data unsatisfactory for determining the pit depth-time curves.
[g] Specimens lost; average pit depths at the close of 6 years.
[h] 1½-inch specimens punctured in less than 8 years.
[i] Specimens buried late; average pit depths at 10 years.
[j] Punctured in 8 years.
[k] Average of the 23 soils with no deletions because of erratic data.

If all specimens were removed and data from them used, the number of observations or, in statistical terms, the size of the sample was 12. In some mildly corrosive soils two specimens were left in the ground so that they could be examined after a longer period of exposure. A few specimens were lost or destroyed, and a few pit measurements have been neglected for reasons stated above. The table includes a column showing the number of specimens which were omitted from the computations and the reason for the omission. A ± sign followed by a number indicates the number of specimens for which no data were available; a + sign and a number indicate that one or more pit measurements were neglected because the values were so much greater than the estimated values for the period that an extremely large standard error would result if the data were included,

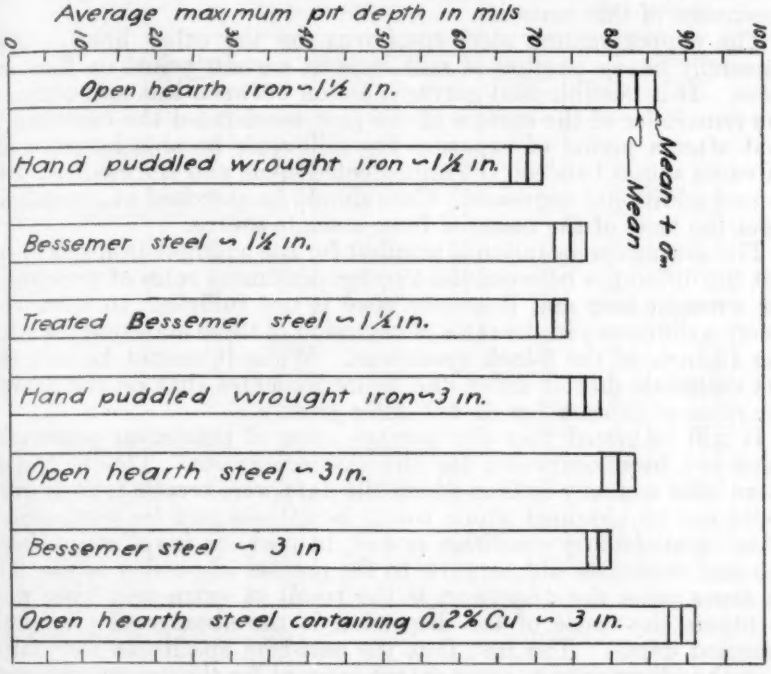

FIGURE 3.—*Average maximum pit depth for twelve years of exposure; twenty-three soils.*

while a — sign indicates that the pit depth was much less than the estimated value. It is possible, therefore, for anyone to revise the table by eliminating the soils from which data were deleted without completely recalculating the table.

At the bottom of the table the average rates of corrosion for most of the soils are given. The differences in the soils are so great that average rates for all soils have little value, except that they permit a comparison of different materials exposed to the same conditions. These averages have been shown graphically in figure 3. Since the pit depths were not adjusted to take account of the areas of the specimens only materials of the same size are strictly comparable.

The figure indicates that there may be a real difference between open-hearth iron specimens and the other 1½-inch wrought specimens, since the difference between the average pit depth of the iron and that of the other 1½-inch specimens is approximately twice the sum of the standard errors of the materials. Similarly, the 3-inch open-hearth steel containing 0.2 percent of copper may corrode at a different rate from that of the steel to which copper was not added. In both cases the reason for the differences may be the character of the surfaces of the specimens employed, and the conclusions might not apply to materials having similar compositions but different surface finishes. In the case of the open-hearth iron the surfaces of the specimens were covered by an almost continuous thin oxide film which broke down in a relatively few places, thus concentrating the galvanic action. A basis for this suggestion is the low losses of weight of the specimens of this material.

The copper-bearing steel specimens, on the other hand, carried unusually heavy patches of mill scale at certain points on their surfaces. It is possible that galvanic action between this mill scale and the remainder of the surface of the pipe accelerated the corrosion, or that after a period of exposure the mill scale became loosened and galvanic action between the unprotected spots and the oxidized areas caused additional corrosion. Care should be exercised in generalizing from the tests of the material from a single source.

The average penetration is smallest for the wrought-iron specimens, but the difference between the average maximum rates of penetration for wrought iron and Bessemer steel is not sufficient to show positively a difference in the rates of corrosion of these materials for either the 1½-inch or the 3-inch specimens. While it cannot be said that the materials do not differ, the figure indicates that on the average the rates of penetration do not differ greatly.

It will be noted that the average rates of maximum penetration have not been computed for the cast specimens. This is because there were so many soils in which the data were erratic that averages could not be obtained which would be satisfactory for comparisons. This unsatisfactory condition is due, in part, to fewer specimens of the cast materials and, in part, to the greater dispersion of the data. In some cases the dispersion is the result of extra-deep pits, while in others the cause of the dispersion is the absence of pits of the expected depth. The fact that the cast-iron specimens were larger than the others may to some extent account for the greater dispersion of their data as well as for the greater maximum pit depths that sometimes appear.

Figure 3 indicates also that the maximum pits are generally deeper on the 3-inch than on the 1½-inch specimens, but table 7 shows that this is not always the case.

3. CORROSIVENESS OF SOILS

Table 7 indicates that so far as the Bureau of Standards data are concerned all of the 1½-inch materials, with the exception of the open-hearth iron, belong to the same family statistically and that all of the 3-inch specimens, except the steel containing copper, are likewise similar. The data for all similar materials for each soil have been combined for the purpose of showing the relative corrosive-

ness of some of the soils which have been used, although some of the soils may not be typical of the soil types indicated.

Table 8 is the result and may be regarded as showing the most dependable values of pit depths to be expected on specimens of the sizes used after 12 years of exposure to the soils listed. The standard deviation, which is also given for each soil, indicates how much a single observation may depart from the average value. According to the theory of probability, 95 percent of a series of observations should not differ from the average by more than twice the standard deviation.

TABLE 8.—*Estimated average maximum pit depths for specimens of wrought iron and steel in certain soils at 12 years*

Soil [a]	1¼-inch specimens				3-inch specimens			
	Number of specimens	Pit depth	Standard deviation	Standard error	Number of specimens	Pit depth	Standard deviation	Standard error
2	28	54.7	14.6	2.8	29	55.3	7.5	1.4
3	36	75.0	10.7	1.8	36	76.6	13.1	2.2
4		74.5	18.0	3.4		97.3	28.9	5.6
7	22	37.0	8.8	1.9	24	45.4	8.0	1.7
8	36	70.4	13.5	2.3	36	90.9	19.9	3.4
11	35	72.9	11.9	2.0	36	79.8	16.9	2.9
14	35	135.4	30.0	5.0	36	108.2	29.2	4.9
16	36	72.8	23.5	4.0	36	81.5	16.3	2.8
17	24	40.5	5.1	1.1	24	46.7	5.0	1.0
18	36	51.7	15.7	2.6	36	61.6	25.3	4.3
19	36	59.3	9.2	1.5	36	69.3	11.3	1.9
22	36	65.9	7.4	1.2	36	64.3	6.2	1.1
25	28	44.0	7.8	1.5	30	53.4	9.9	1.9
28 [b]	24	149.9	22.8	4.8	24	175.3	32.4	6.9
30	29	53.8	9.2	1.7	30	64.4	17.8	5.4
32	36	50.1	10.1	1.7	36	63.9	12.7	2.2
36	30	47.9	8.6	1.6	30	53.2	7.0	1.3
37	36	81.0	24.9	4.2	36	79.0	20.3	3.4
39	35	51.1	48.5	8.3	36	69.3	66.6	11.3
40	36	84.4	17.7	3.0	36	86.1	24.2	4.1
41	30	92.9	29.5	5.5	30	79.1	11.3	2.1
42	36	103.3	22.4	3.8	36	108.4	17.8	3.0
43	36	103.3	36.3	6.1	36	123.9	32.1	5.4
44	30	63.0	9.3	1.7	30	69.6	13.2	2.5

[a] See table 3 for identification of soils.
[b] Specimens exposed for 10 years only.

The number of soils for which data are given in table 8 is very small when compared with the several thousand soil series which have been identified. Nevertheless, a considerable variety of soils is represented and some relation between many other soils and those studied can be found. It is expected that a study of the characteristics of the soils tested will result in a knowledge of why they are or are not corrosive, which knowledge will be applicable to soils in general.

To make the data in table 8 of practical use they should be reduced to some standard area and supplemented by additional information by means of which the time required for the puncture of a pipe wall of some assumed thickness could be computed. Since such an adjustment of the data cannot be made at this time the investigation cannot be regarded as completed.

IV. SPECIAL MATERIALS AND TESTS

1. SUPPLEMENTARY TESTS OF PIPES IN CORROSIVE SOILS

A few soils are of special interest because of their known corrosiveness with respect to some one material, and it seemed desirable to some of those cooperating in the soil-corrosion investigation that several materials be tried out in these corrosive locations primarily for the purpose of finding an inexpensive material suitable for these conditions.

Had the characteristics of underground corrosion been better understood, either more or no specimens would have been placed at these locations, since the number of specimens of one kind exposed to one soil condition is insufficient to permit the estimation of the standard error of the data. However, the results of the tests are recorded in table 9. As in the tables for older materials the wrought specimens appear to corrode at approximately the same rates. In the soils in table 9 high in soluble salts (all soils in the table, except Fairmount silt loam) the cast irons seem to corrode more rapidly than the wrought materials. Fortunately, high concentrations of alkali are confined to relatively small areas, although alkali soils are widely distributed throughout the western half of the country.

TABLE 9.—*Rates of corrosion of wrought and cast pipe buried less than 7 years*

[Average of two specimens]

RATES OF LOSS OF WEIGHT

[In ounces per square foot per year]

Soil [a]	Exposure	A Open-hearth iron	B Wrought iron	N Steel	I Monocast	A and L Pit cast
	Years					
52	1.96	1.56	1.75	1.40	3.79	3.68
54	1.92	.54	.53	.38	.80	.57
68	1.72	1.85	2.09	1.67		2.72
69 [b]	1.83	7.82	7.82	8.13		
112	5.93	3.34	2.84	3.17	(c)	4.70
113 [d]	5.93	4.34	3.67	3.98	(c)	(c)
118	5.93	2.69	2.59	2.51	3.19	4.13

WEIGHTED AVERAGE MAXIMUM RATE OF PENETRATION

[In mils per year]

52	1.96	29.1	29.6	20.9	35.7	25.3
54	1.92	6.3	7.3	2.1	16.7	7.6
68	1.72	22.7	26.5	18.9		30.8
69	1.83	58.4	66.7	77.4		
112	5.93	(f)	26.5	37.5	(f)	44.3
113	5.93	(f)	29.2	38.1		
118	5.93	(f)	25.0	25.0	40.1	40.6

[a] See table 3 for identification of soils.
[b] Six specimens of each material were removed from this soil.
[c] So corroded that a piece of each specimen was broken out when cleaning.
[d] Same soil as number 112 but with more alkali.
[e] So corroded that a piece was broken out of one specimen when cleaning.
[f] Punctured.

Closely related to the data just presented are observations on a few cast materials buried in corrosive soils in 1924. The data are presented in table 10. They are not sufficient to be more than suggestive, but their presentation is believed to be justified by the scarcity of other data on these commonly used materials. Since the elbows (specimens V and S) had no plane surfaces pit-depth measurements were impracticable. The specimens of Monocast iron, I, were coated with the cement which at that time was used to coat the molds. Since the cement came off when the specimens were cleaned the loss due to corrosion could not be determined.

TABLE 10.—*Corrosion of special cast-iron pipe and fittings*

RATES OF LOSS OF WEIGHT

[In ounces per square foot per year]

Soil [a]	Duration of test	Specimens [b]			
		I [c]	V	E	S
	Years				
13	10.16		1.07	1.95	1.32
24	10.63		.10	.38	.11
28	9.60			1.67	1.40
29	10.08		1.18	1.16	1.05
42	10.05		.57	.74	.71
43	10.73		1.09	.81	1.99
45	10.55		2.09	1.89	1.67

WEIGHTED MAXIMUM RATE OF PITTING

[In mils per year]

13	10.16	6.2	11.7		
24	10.63	2.7	4.0		
28	9.60	14.4			
29	10.08	5.2	8.7		
42	10.05	8.0	9.2		
43	10.73	17.6	15.2		
45	10.55	14.7	13.7		

[a] See table 3 for identification of soils.
[b] See table 2 for identification of materials.
[c] These specimens were partially coated with cement in the manufacturing process.

2. BOLTS

Since certain types of joints are bolted, requests have been made from time to time for information as to the best types of bolts for underground use, and as a result a few bolts have been included in the tests at a few sites. Table 11 presents the available data on the corrosion of these bolts. Unfortunately, it has not been practicable to measure pit depth or to test the bolts under the stresses to which they would be subjected in service. Since the data cannot be compared with any other, they are presented in the form of average total losses for each set of bolts rather than as rates of loss of weight. It will be seen from the first part of the table that either sherardizing or coating with lead adds materially to the life of bolts in all soils to which they were exposed. Although no measurements of pits were made, inspection indicated that the corrosion was more nearly uniform on the sherardized bolts. The specimens reported on in the first part of the table have not been exposed to soil action long enough to develop positive differences between the materials.

TABLE 11.—*Corrosion 3/4-inch coated bolts*

MALLEABLE IRON BOLTS

Soil [a]	Number of specimens of each kind [c]	Buried	Total loss of weight, in grams			
			A Decarburized	B Not decarburized	C High strength	D Steel [b]
		Years				
54	2	1.92	2.80	3.86	3.11	3.02
55	2	1.89	3.59	3.65	2.58	2.15
57	2	1.91	3.20	3.69	4.24	4.02
58	2	1.99	7.96	8.98	10.15	9.58
61	2	.95	2.97	2.86	2.93	3.14
62	2	1.93	4.43	5.13	5.67	3.92
63	2	2.04	6.72	6.64	5.17	4.18
Average			4.52	4.97	4.84	4.29

COATED STEEL BOLTS AND NUTS

Soil [a]	Number of specimens of each kind [c]	Buried	Total loss of weight, in grams					
			D [b] Steel		G Sheradized steel		F Lead-coated steel	
			Bolt	Nut	Bolt	Nut	Bolt	Nut
		Years						
13	4	10.16	24.99	8.43	3.20	1.23	6.50	2.02
24	4	10.63	3.04	1.29	2.37	.90	1.43	.78
28	1	9.60	29.11	13.60	19.32	8.63		
29	4	10.08	23.63	9.45	13.45	4.60	18.93	7.92
42	3	10.05	15.30	5.41	4.47	1.80	6.52	2.62
43	4	10.73	37.52	5.47	24.32	8.05	13.05	7.54
45	4	10.55	16.71	5.60	15.19	8.09	42.23	14.40
Average			21.47	7.04	11.76	4.76	14.78	5.88

[a] See table 3 for identification of soils.
[b] Included for comparison.
[c] See table 2 for identification of materials.

3. HIGH-SILICON CAST IRON

Among the materials offered for the original investigation was a cast iron containing approximately 14 percent of silicon. This material is very resistant to many acids. It is not machinable and is easily chipped if not handled with care. Because of this characteristic a number of specimens submitted have been injured and it has been impossible to determine the loss resulting from corrosion. The surfaces of many of the specimens originally contained numerous dimples or pits formed when the specimens were cast. When the specimens were removed it was in many cases impossible to determine whether or not the observed depressions were the result of corrosion, although the general condition of nearly all of the specimens indicates that pitting was improbable. In only one soil, Montezuma clay adobe, soil 28, were the specimens seriously damaged by corrosion. These specimens were split and definitely corroded along the breaks. Corrosion of the specimens of this material in this soil has been observed each time the specimens were removed. Slight rusting or etching has been observed in a few other locations, but in no other soil has the corrosion appeared to be of any practical importance. Table 12 gives the rates of loss of weight for the high-silicon cast iron.

TABLE 12.—*Average rate of loss of weight of specimens of high-silicon cast iron*

Soil [a]	Duration of test	Rate of loss of weight	Soil [a]	Duration of test	Rate of loss of weight	Soil [a]	Duration of test	Rate of loss of weight
	Years	*oz/ft² per year*		*Years*	*oz/ft² per year*		*Years*	*oz/ft² per year*
1	11.65	0.016	23	12.09	0.009	41	11.99	0
2	9.92	.006	24	11.95	.005	42	10.05	.003
4	12.00	.011	26	11.52	.003	43	12.02	.210
5	10.17	.0437	27	10.08	.235	44	11.61	.004
6	10.16	.004	28	9.60	(b)	46	12.00	.002
						47	12.08	.074
7	11.52	.023	30	11.62	.145			
8	11.76	.003	31	10.04	.004			
9	11.51	.008	32	11.66	.011			
10	11.95	.005	33	11.67	.084			
11	11.92	.019	35	10.16	.0736			
14	11.76	.002	36	10.05	.004			
15	10.06	.018	37	10.04	.003			
19	11.63	.001	38	12.01	0			
20	11.65	.015	39	12.00	.019			
22	11.65	.004	40	10.08	.0077			

[a] See table 3 for identification of soils.
[b] Both specimens cracked by corrosion.

4. INFLUENCE OF MILL AND FOUNDRY SCALE

In order to study the influence of the condition of the surface of the material on the rate and distribution of corrosion, specimens of normal material were buried in the same trench with specimens of the same materials from which the original surfaces were removed by a lathe or a grinder which left the surfaces bright. Here, again, the need for economy made it impracticable to use a sufficiently large number of specimens to obtain a very definite result.

Table 13 shows the result of the experiment. Results from copper steel and lead-coated steel are included because it is desirable to compare the data on these specimens with data on specimens belonging to the test without reproducing the latter data.

TABLE 13.—*Effect of mill and foundry scale on corrosion*

(Period of exposure was approximately 8 years)

RATES OF LOSS OF WEIGHT

[In ounces per square foot per year]

Soil [a]	Cast iron				Steel			Wrought iron		
	Pit		deLavaud							
	A [b] Normal	MC Machined	C Normal	MD Machined	C +1.5% copper	P Normal	M Polished	Lead coated	K Normal	D Ground
13	1.12	1.29	0.05	1.10	1.13	1.70	1.51	0.18	1.12	1.01
24	.11	.13	.17	.16	.21	-------	-------	.78	.22	.18
26	3.94	-------	1.14	-------	-------	-------	-------	1.09	-------	-------
29	2.31	.99	5.28	1.27	1.41	1.21	1.06	.61	1.18	1.22
42	.70	.43	.59	.47	.81	.89	.94	.44	.88	.80
43	1.08	1.00	3.08	1.20	.90	.86	1.14	.77	.67	.67
45	3.50	-------	3.55	2.59	3.24	2.64	2.26	1.27	2.51	2.17
Ratio [c]	-------	3-5	-------	5-6	2-5	-------	3-5	5-5	-------	4-6

[a] See table 3 for identification of soils.
[b] See table 2 for identification of materials.
[c] Ratio of cases of superiority to total number of cases of comparison.

TABLE 13.—*Effect of mill and foundry scale on corrosion*—Continued

RATES OF PENETRATION

[In mils per year]

Soil	Cast iron				Steel			Wrought iron		
	Pit		deLavaud							
	A Normal	MC Machined	C Normal	MD Machined	C +1.5% copper	P Normal	M Polished	Lead coated	K Normal	D Ground
13	17.8	12.8	7.8	9.1	16.7	19.3	15.3	6.5	11.9	11.1
24	3.6	3.2	3.8	2.4	3.7	-------	-------	3.3	4.7	3.8
28	20.4	-------	6.8	-------	-------	-------	-------	9.1	-------	-------
29	11.4	5.0	10.7	8.9	7.0	10.5	9.8	7.8	6.3	7.3
42	17.9	15.9	7.0	8.9	10.2	8.8	10.0	7.4	10.3	9.4
43	14.1	5.2	27.5	11.5	19.9	10.8	8.1	19.4	15.3	9.7
45	22.3	-------	14.3	15.7	26.1	16.6	13.0	10.1	12.9	18.2
Ratio [a]	-------	5:5	-------	3:6	2:5	-------	4:5	4:5	-------	4:6

PITTING FACTOR

13	9.4	5.8	9.5	4.9	9.6	7.4	6.6	16.8	6.8	7.0
24	17.7	14.3	13.8	8.6	11.5	-------	-------	28.0	13.7	13.7
28	3.0	-------	3.5	-------	-------	-------	-------	5.5	-------	-------
29	2.9	2.9	1.3	4.1	3.3	5.7	6.0	8.6	3.4	3.8
42	17.0	21.9	6.7	11.3	8.2	7.5	7.3	13.1	7.5	7.5
43	7.9	2.9	4.9	5.3	14.4	8.3	4.2	15.6	16.2	9.5
45	3.9	-------	2.4	3.9	5.3	4.1	3.7	5.3	3.3	5.3
Ratio [a]	-------	3-5	-------	2-5	1-5	-------	4-5	0-5	-------	1-6

[a] Ratio of cases of superiority to total number of cases of comparison.

In the beginning of the discussion of this table it should be pointed out that the data are too few to justify positive conclusions as to the relative merits of the two types of pipe surfaces. Nevertheless, they are of considerable interest because they throw a little light on a question often discussed with no more than opinions as bases for discussion. Since the results in some soils show trends opposite to those in other soils and since the losses in some soils are so much greater than in others that averages would be meaningless, an attempt to show the trend of the data has been made by giving the ratio of the cases in which a material is superior to the total number of possible comparisons. Several comparisons can be made. Turning first to the data on machined and unmachined pit-cast iron, it appears that removing the outer skin or surface of this material tends to reduce both the loss of weight and the pit depths as well as to make the corrosion more uniform. This is a little surprising since the suggestion has been frequently advanced that the surface of cast-iron pipe has a siliceous scale which retards corrosion. However, since the sand mold in which the pipe was cast was coated with blacking, the metal absorbed little or no silica from the mold. Chemical analyses of cast surfaces showing high silicon content may be explained by the occasional imbedding of a particle of sand in the pipe surface.

A comparison of the unmachined and machined deLavaud cast iron shows the same tendency toward less corrosion of the machined specimens, though to a less marked extent. The semipolished steel appeared better with respect to loss of weight, pit depths, and pitting factor in three of the five soils. This result might be attributed to chance if it were not in accord with the results for other materials. The rough-ground wrought iron was superior to the ordinary material with respect to loss of weight in 5 out of 6 soils, though the differences were in all cases rather small. The ground wrought-iron specimens

showed shallower maximum pits than the ordinary wrought iron in 4 of the 6 soils. The differences are small in 4 soils but large in 2 soils.

Considering the table as a whole, the character of the surface of the pipe with respect to the presence or absence of mill or foundry scale appears to have had an effect on the corrosion of the metals tested. This effect is small in comparison with the effects of soil characteristics on underground corrosion.

Table 13 indicates also that the addition of 1.5 percent of copper to steel did not increase its resistance to corrosion.

The specimens which were coated with lead lost less weight than did the uncoated steel specimens in all soils, and in 5 of the 6 soils the pit depths were less on the lead-coated pipes. In soil 43, a tidal marsh, the lead-coated specimens showed much deeper pits than the uncoated specimens. This is in agreement with other tests of the lead-coated specimens in this soil.

5. EFFECT OF AREA AND DIAMETER OF SPECIMENS ON THE RATE OF PENETRATION

Early in this soil-corrosion investigation [9] it was observed that the average maximum pit for the 1½-inch specimens was less than the corresponding average maximum pit on the 3-inch specimens of the same material, and to partially compensate for this the pit depths were weighted by averaging the deepest pits on the 2 specimens of 1½-inch material, the 2 deepest pits on each 2- and 3-inch specimen, and the 4 deepest pits on each 6-inch specimen. Since for one 6-inch material (deLavaud cast iron) there were 2 specimens, the reported maximum pit depth for this material was actually the average of 8 pit depths, while the reported maximum pit depth for each material represented by 1½-inch specimens was the average of 2 pit depths. This procedure brought the results of observations on different sizes of the same material into closer agreement and has been followed in all subsequent reports.

In order to obtain additional data on the relation between the area of the specimens from which the maximum pit was chosen and the magnitude of the result obtained, specimens of each of two materials differing in size were buried in 13 soils in 1932. The dimensions and numbers of the specimens were so chosen that the total areas of each of the groups of specimens were approximately the same. Thus, in each soil there were 2 specimens of steel 2 inches in diameter and 10 inches long; 2 specimens each of steel and cast iron 3 inches in diameter and 6 inches long; 2 specimens of cast iron 1¼ inches nominal inside diameter and 13 inches long; and 1 specimen of 6-inch cast iron, 6 inches long. The 4 deepest pits on each of the 6-inch specimens and the 2 deepest pits on each of the other specimens were measured. In table 14 the rates of penetration have been computed in three ways: (1) from the single deepest pit on the combined area for each material in a given soil; (2) from the average of the single deepest pits for each specimen of each material except the 6-inch cast iron for which there was only 1 specimen; and (3) the weighted average pit depth computed from the 4 deepest pits on the 6-inch specimens and the 2 deepest pits on each of the other sizes, i. e., the average of 4 pits in each case. This is the method used in reporting weighted maximum pit depths in this and earlier reports.

[9] Logan and Grodsky. *Soil corrosion studies 1930.* BS J. Research 7, 5 (19) RP379, 10c.

TABLE 14.—*Effect of the method of determining the value of the deepest pit*

[Total pit depths on specimens buried for the purpose of studying the relation of pit depth to the area exposed. The total area is approximately the same for each diameter of specimen. There were two specimens of each size, except the 6-inch cast iron]

Soil [a]	Duration of test	Steel pipe						Cast-iron pipe						
		2 inch (N) [b]			3 inch (M′)			1¼ inch (G)			3 inch (M)		6 inch (L)	
		Single max	Avg max	Wtd max	Single max	Avg max	Wtd max	Single max	Avg max	Wtd max	Single max	Avg max	Wtd max	Single max	Wtd max
	Years														
51	1.98	101	82	80	63	49	44	138	117	102	110	78	73	87	78
53	1.96	37	37	32	56	52	50	47	42	41	54	45	39	32	27
55	1.89	42	41	39	54	48	46	50	47	45	40	36	35	57	42
56	1.99	26	20	18	65	52	48	39	36	35	55	52	49	56	38
57	1.91	34	32	30	36	30	27	53	52	46	39	38	33	49	38
58	1.99	20	18	18	31	30	27	28	27	24	45	35	34	58	54
60	1.92	55	37	36	49	34	33	58	53	51	90	82	73	90	65
61	.95	13	10	9	30	18	17	50	43	34	5	5	5	5	5
62	1.93	68	62	55	57	50	49	67	64	64	64	47	46	90	83
63	2.04	21	15	13	41	36	34	29	24	22	50	44	42	62	60
64	1.91	138	130	127	134	133	129	135	123	121	215	211	208	265	225
65	1.91	43	40	39	75	66	65	53	50	49	101	93	88	145	102
66	1.92	71	66	61	120	110	106	75	60	53	74	69	66	91	75
Average	------	51.5	45.4	42.8	62.4	54.5	51.9	63.2	56.8	52.8	72.5	64.2	60.8	83.6	68.6
Standard error	------	9.9	9.2	9.0	8.8	9.0	8.9	9.7	8.4	8.0	14.2	13.9	13.9	17.8	14.9

[a] See table 3 for identification of soils.
[b] See table 2 for identification of materials.

The corrosivities of the soils differ so greatly that the averages and standard errors recorded at the bottom of the table have little significance with respect to corrosion, but since all materials were exposed to the same soils the averages are of interest even though the size of the standard error indicates, from a statistical standpoint, that the relative magnitudes of the averages may be accidental. It will be noted, first, that for each type of specimen the single maximum pit depth is usually considerably greater than the average values. This is, of course, the result of unequal corrosion at different points on the pipe surfaces and at once raises a question as to how much greater the maximum pit would be if a length or a mile of pipe were taken as the unit for observation. At present this question cannot be answered, but there are definite indications that as the area under observation is increased the depth of the deepest pit also increases. This means that the values given for pit depths in the reports on underground corrosion by the Bureau of Standards should be increased if the maximum pit depth on an area greater than that of the unit used in the Bureau of Standards reports, i. e., that of a 1½-inch pipe, 5 inches long, is desired. This problem is being investigated further.

Turning to the question of the effect of using a number of pit depths proportional to the areas of the specimens for the purpose of comparing pit depths on specimens of different sizes, table 14 affords three opportunities for comparison. It will be seen that if either the average maximum or the weighted average maximum pit depths on the 2-inch specimens, N, are compared with the corresponding pit depths on the 3-inch specimens, M′, the average values for the

specimens having the larger diameter are greater, although the areas of the two kinds of materials are approximately the same. Similarly, the averages for the 3-inch cast iron are greater than for the 1½-inch cast iron, and the weighted maxima for the 3-inch and 6-inch cast-iron specimens show the same trend. The averages for the several materials are shown in figure 4.

While, as previously stated, the standard errors indicate that no positive differences between the averages have been demonstrated,

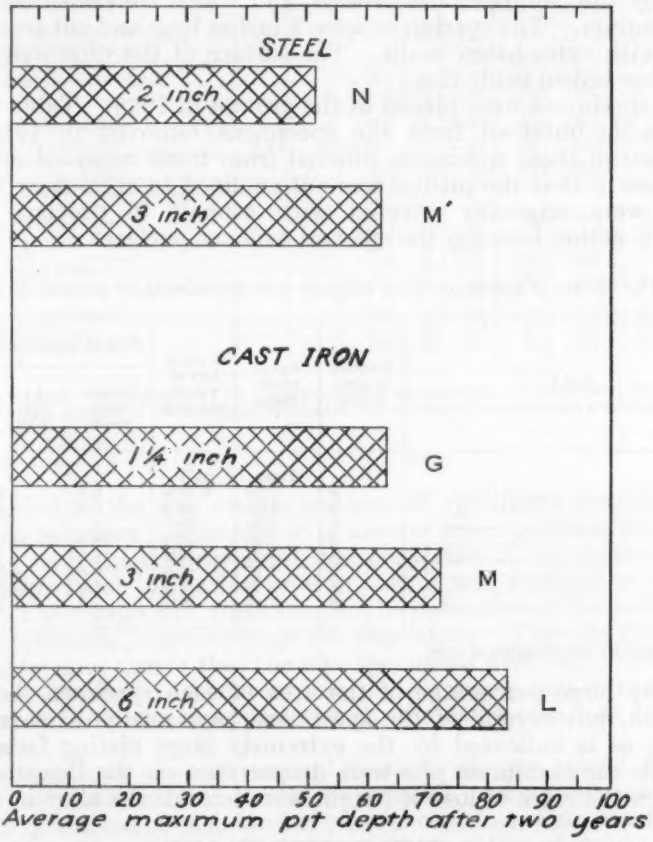

FIGURE 4.—*Effect of pipe diameter on depth of maximum pit.*

the fact that the trends in all cases are in the same direction carries at least a suggestion that the shape of the individual pipe sections, as well as the total area for which the maximum pit depth is computed, should be considered. The relation of the value of the maximum pit depth to the area and dimensions of the unit is important not only in the study of the Bureau of Standards data, but in the interpretation of inspection data which may be obtained for the purpose of determining the condition of operating pipe lines.

V. TESTS OF MATERIALS IN CORROSIVE SOILS

1. TUBES CONTAINING 26 PERCENT OF CHROMIUM

The resistance of the alloys of iron and chromium to atmospheric corrosion has raised questions as to the desirability of adding small amounts of chromium to iron or steel in the manufacture of pipes for underground use. The first attempt by the Bureau of Standards to study this question was the burial of a few specimens of tubing made by the Mannesmann process, and which contained 26 percent of chromium. The specimens were 6 inches long and cut from 1-inch tubes with extra-heavy walls. The surface of the pipe was covered by a thin brown oxide film.

The specimens were placed in the ground in 1926. Table 15 gives the results obtained from the specimens removed in 1934. The condition of these specimens differed from those removed on former occasions in that the pitting was not confined to areas near the ends which were originally covered with asphalt to prevent possible galvanic action between the cut and oxidized surfaces.

TABLE 15.—*Rates of corrosion of an alloy of iron containing 26 percent of chromium*

Soil [a]	Number of specimens	Age of specimens	Rate of loss of weight per year	Rate of penetration		Average pitting factor
				Single maximum	Avg. maximum	
		Years	oz/ft²			
13	3	7.96	0.0054	0.0	0.0	1
23	3	7.96	.0208	6.6	5.9	182
24	3	7.94	.0067	0	0	1
28	6	7.96	.0163	23.7	14.0	552
29	3	7.97	.0352	10.2	8.2	149
42	6	7.97	.0203	6.8	4.8	151
43	6	7.95	.6747	30.0	24.5	23
45	6	7.95	.0117	3.0	1.2	68

[a] See table 3 for identification of soils.

A very large percentage of the area of each specimen showed no corrosion, but several of the specimens have sustained severe local pitting, as is indicated by the extremely large pitting factors. In two soils the maximum pits were deeper than on the Bessemer steel, although the rates of loss of weight were less for the alloy in all soils.

2. PIPE BURIED IN 1932

Table 16 shows the analyses of the ferrous materials buried in 1932, as furnished by their producers. The dimensions of the specimens are given in table 2.

TABLE 16.—*Analyses [a] of ferrous materials (in percent)*

[See table 2 for dimensions of specimens]

Identification letter	Material	Gr	C. C.	T. C.	Si	Mn	S	P	Cr	Ni	Cu
A	Puddled wrought iron [b]	------	------	0.026	0.100	0.029	0.018	0.160	------	------	------
B	------do.[c]	------	------	.02	.125	.041	.018	.106	------	------	------
C	Low alloy cast iron	2.0	0.5	3.5	2.5	.7	.05	.4	0.3	0.15	------
D	Cu-Ni steel pipe	------	.14	.14	.19	.21	------	------	------	2.47	1.08
E	High alloy cast iron	------	------	2.98	2.13	1.0	------	------	2.61	15.0	6.58
F	Sand-coated cast iron } avg	2.9	.6	3.5	1.85	.5	.75	.7	------	------	------
G	Rattled cast-iron pipe }										
H	Cu-Mo open-hearth iron pipe [d]	------	------	.04	.05	.32	.027	.016	------	------	.52
I	Special cast-iron pipe	------	------	2.53	1.43	.28	.077	.128	------	------	.51
J	------do	------	------	2.9	2.04	.83	.060	.248	------	------	.62
K	Cr-Ni alloy sheet	------	.08	.08	.33	.44	.022	.015	17.2	8.95	------
L	6-in. cast-iron pipe } avg	2.92	.83	3.75	1.49	.47	.08	.62	------	------	.07
M	3-in. cast-iron pipe }										
N	Low-carbon tube	------	------	.15	------	.49	.030	.013	------	------	------
P	5% Cr tube	------	------	.13	------	.46	.025	.012	5.05	------	------
R	Cr-Ni alloy tube	------	------	.05	.28	.46	.011	.015	17.52	8.85	------
S	Cr-Mn alloy sheet	------	------	.07	.48	9.44	------	------	17.78	------	.74
T	------do	------	------	.06	.40	6.09	------	------	17.76	3.83	.95
U	Cr-alloy sheet	------	------	.065	.28	.38	.017	.011	11.95	.482	.025
V	------do	------	------	.070	.34	.36	.015	.014	17.08	.092	.021
W	Cr-Ni alloy sheet	------	------	.093	.42	.36	.017	.008	18.69	9.18	.016
X	Cr alloy tube	------	------	.12	.277	.42	.017	.016	17.72	.287	------
Y	Cr-Ni alloy sheet	------	------	.144	.59	1.80	.011	.015	22.68	12.94	.021

[a] These analyses were furnished by the manufacturers of the materials. In some cases they may represent the average analyses of the materials represented rather than of the specimens submitted for test.
[b] Oxide and slag, 2.560%.
[c] Oxide and slag, 2.681 %.
[d] Molybdenum, 0.15%.

Included in the test are several sets of specimens placed there to serve as reference specimens or to answer some question not dealing directly with the corrosion-resisting properties of the material. The test differs from the earlier ones in that it was confined to corrosive soils. The results will, therefore, not be indicative of the performance of the materials under average soil conditions. The test differs from the earlier ones also in that the pipe specimens were laid on their sides, had the ends closed to prevent internal corrosion, and were so chosen that on each specimen approximately the same area was exposed to the soil.

The specimens of stainless-steel sheet metal were placed on edge in order that both surfaces should be exposed to the same condition.

Two specimens of each kind of pipe, except two, were removed from each of 14 soils in 1934. The average rates of loss of weight for these specimens are recorded in table 17. While in a large majority of cases the two specimens of the same material in the same soil agree quite closely with respect to loss of weight, there are a few cases in which one specimen lost approximately twice that of its mate.

TABLE 17.—*Rates of loss of weight of ferrous pipe buried in 1932*

[Ounces per square foot per year]

Soil [a]	Duration of test	Puddled wrought iron A	Puddled wrought iron B	Low-carbon tube N	5% Cr tube P	18% Cr alloy tube X	18% Cr, 8% Ni alloy tube R	Cu-Ni steel D	Cu-Mo open-hearth iron H	Cast iron G	Low-alloy cast iron C	Special-process cast iron I	Special-process cast iron J	High-alloy cast iron E
	yr													
51	1.98	5.93	4.14	3.75	3.23	------	------	2.39	3.12	5.60	7.62	7.50	7.43	2.31
53	1.96	1.77	1.75	1.37	.69	------	------	1.10	1.41	2.40	1.97	1.55	1.57	.61
55	1.89	1.51	1.52	1.28	.61	------	------	.88	1.04	1.42	1.81	1.48	2.07	.40
56	1.99	1.76	2.22	2.03	1.26	------	------	1.67	1.17	4.75	3.61	2.58	2.56	1.67
57	1.91	1.82	1.65	2.33	2.31	0.001	0.000	1.49	2.72	1.74	2.25	2.75	2.96	.18
58	1.99	1.76	1.60	1.85	.91	.002	.001	1.77	1.45	2.92	4.54	2.32	1.85	.42
60	1.92	2.96	2.62	3.24	2.24	------	------	2.53	2.54	5.50	4.69	5.12	4.07	2.17
61	.95	1.38	1.29	.86	.82	------	------	1.25	.98	1.12	1.29	.99	1.07	.28
62	1.93	1.56	2.09	2.12	1.25	.001	.000	1.41	1.92	3.48	3.30	3.39	3.51	.86
63	2.04	1.48	1.30	1.88	.65	.017	.012	.77	1.22	1.87	1.52	1.38	2.25	.28
64	1.91	5.96	6.94	6.62	7.32	.264	.001	3.40	8.44	6.59	7.52	8.09	8.34	2.32
65	1.91	4.16	3.22	3.87	3.78	------	------	2.61	3.92	5.40	6.76	6.24	5.76	.80
66	1.92	4.47	4.06	4.02	4.03	------	------	2.66	4.57	3.13	4.31	2.64	3.14	1.60
67	2.02	4.28	5.67	10.65	3.68	.003	.000	8.16	3.84	13.25	10.63	15.00	12.18	8.74
Average	-----	2.91	2.86	3.27	2.34	.048	.002	2.29	2.74	4.23	4.42	4.36	4.20	1.62
Avg 67 omitted	-----	2.77	2.65	2.71	2.24	------	------	1.84	2.65	3.53	3.94	3.54	3.58	1.07

[a] See table 3 for names of soils.

So many figures are presented in the table that it is difficult for a reader to grasp the significance of the individual rates. For this reason the average rate has been computed for each material in all soils, although it is recognized that the dispersion of the values going to make up the average is so great that the average rate has little practical significance, and that the relative merits of the materials might be changed if the tests were extended to other soils. Thus for most of the materials the average rate of loss of weight is markedly affected by the specimens that were removed from soil 67. For example, if the data for this soil were omitted the average rate of loss for Bessemer steel would be reduced from 3.3 oz/ft²/yr to 2.7 oz/ft²/yr, while for copper-molybdenum-iron alloy the change is much less, i. e., from 2.74 oz/ft²/yr to 2.65 oz/ft²/yr. It should be remembered also that when the specimens have been exposed for a longer time their rates of corrosion may be relatively different.

Table 18 shows the rates of maximum penetration for the ferrous pipe materials buried in 1932. The average maximum rates of penetration are shown graphically in figures 5 and 6. In the latter figure the rates are for only the soils to which all the materials in the figure were exposed.

The standard error which is given for the averages of all specimens removed from each soil is so large that small differences in the averages for 10 materials are not significant. Thus, the table indicates that the 2 sets of wrought-iron specimens are so nearly alike that any differences between the two materials cannot be determined from the data. Likewise, the addition of 5 percent of chromium to low-carbon steel did not produce a positive difference between the two materials.

TABLE 18.—*Rates of maximum penetration of ferrous pipe buried in 1932*

[Average maximum rate of penetration, in mils per year]

Soil [a]	Duration of test	Puddled wrought iron A	Puddled wrought iron B	Low-carbon tube N	5% Cr tube P	18% Cr alloy tube X	18% Cr, 8% Ni alloy tube R	Cu-Ni steel D	Cu-Mo open-hearth iron H	Cast iron G	Uncleaned cast iron F	Low-alloy cast iron C	Special-process cast iron I	Special-process cast-iron J	High-alloy cast iron E
	Years														
51	1.98	25.2	30.0	41.4	34.8	-----	-----	34.1	39.7	59.3	45.4	56.9	51.5	53.3	15.4
53	1.96	17.3	15.3	18.9	23.5	-----	-----	11.7	27.8	21.4	24.2	19.9	15.6	27.6	15.1
55	1.89	21.4	22.5	21.7	22.5	-----	-----	17.2	31.7	25.1	25.1	13.8	15.1	19.0	15.9
56	1.99	11.1	12.3	9.8	29.1	-----	-----	10.1	10.3	18.3	20.6	16.3	10.8	14.8	21.4
57	1.91	9.2	10.5	16.8	13.6	8.1	0.0	16.2	26.2	27.2	25.4	42.7	21.7	25.7	13.6
58	1.99	10.1	8.8	9.0	17.8	5.0	6.3	11.6	10.6	13.3	17.3	22.4	20.6	14.1	25.1
60	1.92	12.8	12.2	19.3	17.2	-----	-----	14.3	14.1	27.3	25.5	18.0	19.5	19.5	12.5
61	.95	17.9	10.5	11.1	10.5	-----	-----	12.1	15.3	45.3	25.8	15.8	31.6	27.9	37.9
62	1.93	25.4	36.0	32.1	26.7	6.2	6.0	21.8	37.0	33.4	36.0	41.7	52.1	35.2	22.3
63	2.04	13.7	8.1	7.4	21.1	62.0	20.8	11.8	14.5	11.5	18.4	4.7	10.0	25.0	11.0
64	1.91	53.1	61.5	68.3	65.2	80.6	4.2	51.0	80.1	64.7	68.6	74.6	70.9	62.6	14.4
65	1.91	28.3	34.3	20.7	35.6	-----	-----	21.5	48.9	26.2	24.3	30.6	29.3	30.1	13.4
66	1.92	45.6	42.4	34.4	44.5	-----	-----	29.9	57.8	31.2	29.2	35.2	29.7	27.9	13.8
67	2.02	49.7	48.8	76.2	31.9	8.9	3.2	50.0	32.2	79.0	63.9	58.9	63.6	53.2	46.3
Average	------	24.3	25.2	27.7	28.1	-----	-----	22.4	31.9	34.5	32.1	32.3	31.6	31.1	19.9
Standard error	------	4.0	4.6	5.7	3.8	-----	-----	3.7	5.4	5.4	4.3	5.5	5.3	4.0	2.8

[a] See table 3 for names of soils.

Desire for economy prevented the burial of the two materials containing 18 percent of chromium in all of the soils and for this reason the averages for these materials cannot be compared with those for other materials. Comparing the low-carbon steel without chromium with a material which is similar except for the addition of 18 percent of chromium, it appears that the latter material is probably somewhat better in two of the soils, much better in one, and much worse in the fifth. It is not possible to determine whether or not these differences are significant. The addition of 8 percent of nickel to the iron-chromium alloy seems to result in a definite improvement in the material with respect to loss of weight and rate of maximum penetration. The beneficial effect of the nickel is also indicated by the data for copper-nickel steel and high alloy cast iron.

With the exception of the last-named material all of the cast materials seem to corrode at approximately the same rates. While the data in the table taken at their face values indicate that some materials are relatively more suitable for some soils than for others the number of observations is too small and the time of exposure is too short to justify more than very tentative deductions as to the relative merits of the materials.

3. SHEET METAL CONTAINING CHROMIUM

Several varieties of this class of alloys have been included at 7 of the sites for testing corrosion-resistant materials. If the chemical constituents of the materials were the only factors affecting their corrosion a correlation of the analyses of the materials with their rates of corrosion might lead to the development of a more corrosion-resistant

material. It is possible, however, that the heat treatment of the material and the roughness of its surface have important effects. Unfortunately, the surface finish of the specimens differed considerably and since the materials came from three sources the heat treatments may have differed also.

Table 19 records the corrosion data for the sheet specimens removed in 1934. The number in parentheses immediately under the

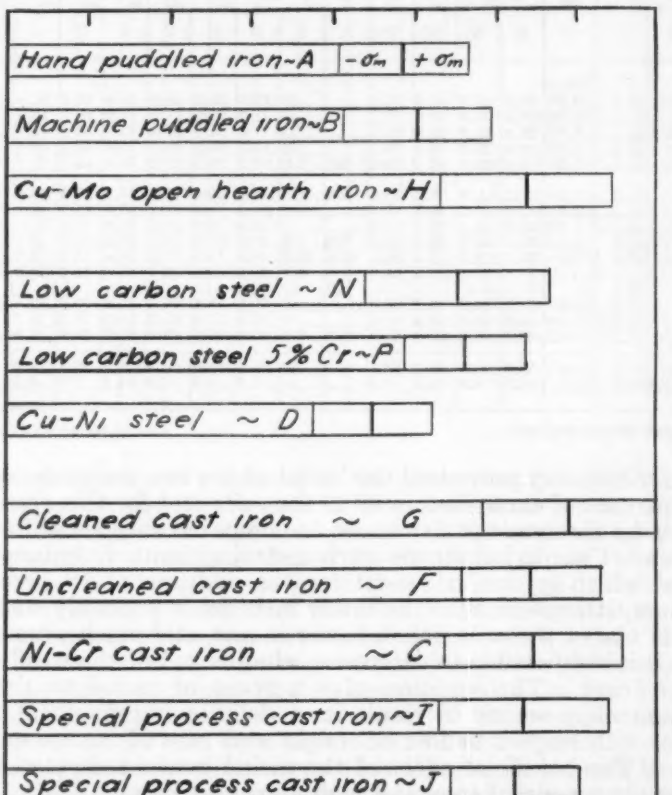

FIGURE 5.—*Rates of penetration of several ferrous materials exposed for two years to fourteen corrosive soils.*

letter designating the material indicates the number of specimens removed from any one soil. The specimens were so thin that in 3 soils most of them were punctured. For this reason the data on rates of penetration are not as useful as similar data on pipes. Table 20 repeats part of the data in table 19 and gives the standard error for the repeated data. From the standard error the dependability of the data may be judged. Where the losses are very small it is more diffi-

cult to determine the average loss with precision but this only accounts, in part, for the standard error which, in one case, is nearly as large as the rate of loss of weight. An examination of the specimens would show that while in most cases most of the specimens of any material in one soil behaved similarly, occasionally an exceptionally good or bad specimen is to be found. While the pitting factor has not been computed it can safely be said to be very large in all cases.

The rates of loss are so different for the same material in different soils that in most cases the rate for one of the soils would almost determine the average for all of the soils, and on this account the rates of loss have not been averaged.

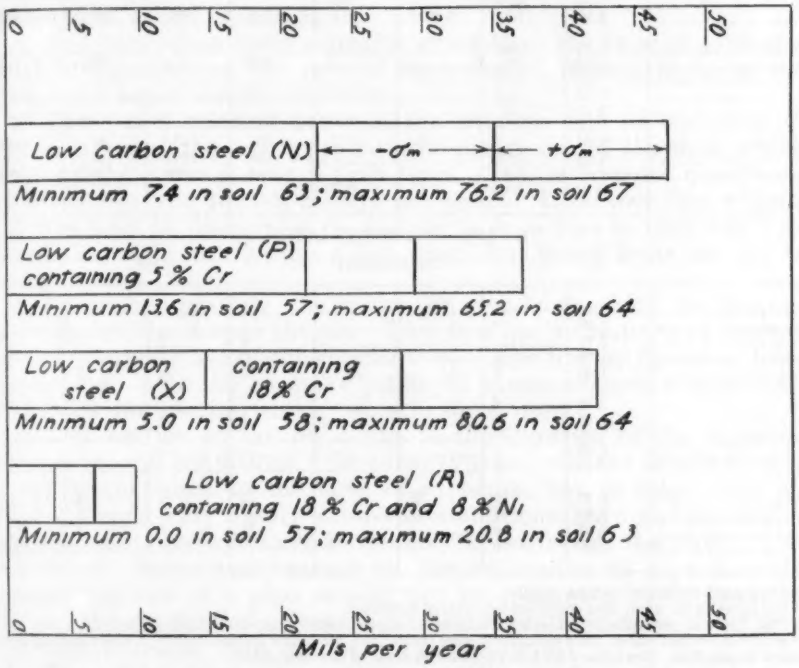

FIGURE 6.—*Rates of penetration of alloy steels exposed for two years to six soils.*

For all soils concerned except two, the specimens containing the least chromium corroded the most. Soil 64 was the most destructive with respect to the materials containing very little nickel, while soil 65 was more corrosive than soil 64 with respect to all but one class of the specimens containing considerable amounts of nickel. This relation is not supported by the data for specimen K (table 19), but since the 2 specimens of this material in either of the above soils differed very greatly in their losses the data for material K are not very helpful. It is rather surprising that the material containing the most chromium and nickel corroded distinctly more than one of the other materials in every soil to which it was exposed.

TABLE 19.—*Average rates of loss of weight and maximum penetration of iron-chromium alloy sheets*

RATES OF LOSS OF WEIGHT

[Ounces per square foot per year]

Soil [a]	Exposure	K [b] (2) [c] 17% Cr, 9% Ni, 0.4% Mn	S (2) 18% Cr, 0% Ni, 9% Mn	T (1) 18% Cr, 4% Ni, 6% Mn	U (5) 12% Cr, 0.5% Ni, 0.4% Mn	V (5) 17% Cr, 0.1% Ni, 0.4% Mn	W (5) 19% Cr, 9% Ni, 0.4% Mn	Y (5) 23% Cr, 13% Ni, 1.8% Mn
	Years							
51	1.98	0.0046		0.0046				
53	1.96	.0022		.0022				
55	1.89				0.0004	0.0018	0.0002	0.0011
56	1.99	.0007		.0007				
57	1.91	.0003	0.0013	.011	.052	.027	.0003	.0018
58	1.99	.0007						
60	1.92	.0015			.0006	.0004	.0003	.0015
61	.95	.0010						
62	1.93	.0007						
63	2.04	.017						
64	1.91	.0076	.048	.057	.35	.28	.0010	.0015
65	1.91	.0026			.068	.065	.0055	.019
66	1.92	.0004			.039	.028	.0002	.0015
67	2.02	.0005	.0003	.0025				

RATES OF PENETRATION

[Mils per year]

51	1.98	[d] H						
53	1.96	0						
55	1.89				0	3	6	3
56	1.99	0						
57	1.91	0			H	14	17	0
58	1.99	0						
60	1.92	0			1	0	1	1
61	.95	0						
62	1.93	0						
63	2.04	H						
64	1.91	9	H	H	H	H	4	5
65	1.91	H			H	H	H	H
66	1.92	0			H	0	5	3
67	2.02	0	2	0				

[a] See table 3 for identification of soils.
[b] See table 16 for name and complete analysis of materials.
[c] The figure in parentheses indicates the number of specimens removed from each test site.
[d] H indicates that one or more specimens were punctured, rendering the computation of the rates of penetration impossible. See table 2 for thicknesses and areas of the specimens.

TABLE 20.—*Rates of loss of weight for four varieties of iron-chromium alloy sheets (in ounces per square foot per year)*

[Age approximately 2 years]

Soil [a]	U [b] Cr 12%, Ni 5%, Mn 4%		V Cr 17%, Ni 1%, Mn 4%		W Cr 19%, Ni 9%, Mn 4%		Y Cr 23%, Ni 13%, Mn 1.8%	
	Average loss	Standard error	Average loss	Standard error	Average loss	Standard error	Average loss	Standard error
55	0.0004	0.00018	0.0018	0.0010	0.0002	0.0001	0.0011	0.0001
57	.052	.023	.027	.0060	.0003	.0001	.0017	.0004
60	.0006	.00009	.0004	.0002	.0003	.0001	.0015	.0002
64	.35	.03012	.28	.029	.0010	.0004	.0015	.0007
65	.068	.00065	.065	.0053	.0060	.0046	.019	.0119
66	.039	.0089	.028	.011	.0002	.00003	.0015	.0003

[a] See table 3 for identification of soils.
[b] See table 16 for complete analyses of materials.

IV. SUMMARY

Since, in certain localities at least, the field work of the original soil-corrosion investigation has been completed, it may be well to include in the summary of the work on the 1934 specimens presented in this report, a statement of all of the more important facts which the entire investigation has brought out. Some of these statements can only be confirmed by references to the earlier soil-corrosion reports referred to in this paper.

1. Serious corrosion of underground pipes frequently occurs in the absence of stray currents from electrical generating stations. Electrical currents which did not originate in power houses have been observed on many pipe lines.

2. Soil conditions have a greater effect than the type of pipe material in determining the rate of corrosion of ferrous pipes in the absence of stray electric currents.

3. There is a relation between the average rate of corrosion of iron in soil and the soil type, but the dispersion of the data which make up the average rate is very large. This is because conditions within a soil type are not always the same. It follows that while a soil type may be designated as noncorrosive, a pipe in that soil may develop a single leak within a few years, but many leaks are not to be expected.

4. Generally speaking, the larger the area from which the deepest pit is chosen the deeper the pit. This fact has an important bearing on the determination of the condition of a pipe line by means of local inspections. In order to make pit-depth measurements comparable, similar methods of inspecting pipes must be used.

5. The relation of the pit depth to the duration of the exposure depends on soil conditions. In some types of soil the penetration is nearly proportional to the time of exposure, but in other soils pit depths deepen very slowly after soil conditions have become stable and corrosion products have formed on the surface of the pipe. This fact has an important bearing on the estimation of pipe life. In general, the life of a pipe should not be estimated solely from its age and the depth of the deepest pit because in most soils the rate of corrosion decreases with the time of exposure.

6. The distribution of corrosion usually tends to become more uniform as the age of the pipe increases.

7. Under similar soil conditions the wrought iron and steel specimens corroded at approximately the same rates during the first 12 years of exposure. In many of the soils under tests, especially those in the arid regions containing large amounts of soluble salts, the rate of corrosion of cast iron is somewhat greater than that of steel. From a practical standpoint the thickness of the material and the nature of the corrosion products should also be taken into account in determining the material most suitable for some soil condition.

8. The addition of copper alone to steel does not increase its resistance to the action of most soils.

9. The rate of corrosion of pipe underground is not greatly affected by the removal of mill or foundry scale, but the available data seem to indicate a slight reduction in loss and penetration when the scale is removed.

10. No material has been found which will withstand corrosion under all soil conditions.

The following tentative deductions are based on a relatively few specimens exposed to 14 corrosive soils for approximately 2 years.

1. The addition of chromium to steel reduces the rate of loss of weight but does not prevent serious localized pitting in all soils. The pitting seems to be worst in soils containing chlorides.

2. The addition of nickel to iron-chromium alloys seems to improve their resistance to underground corrosion.

3. An alloy containing 18 percent of chromium and 8 percent of nickel corroded less than an alloy containing more of these elements.

The work of cleaning the specimens upon which this report is based was undertaken at a time when the number of men available for the work was less than half that formerly available, although the number of specimens to be handled had been approximately doubled. Moreover, with the exception of the author, no one was left who was entirely familiar with the specimens or the processes involved in cleaning them. The work was undertaken by Robert Hobbs with the assistance of one laborer. A little later a group of pipe manufacturers contributed funds for the employment of labor for cleaning the specimens. This was supplemented by the part-time assistance of a man from Federal relief rolls. A large part of the computations have been made and checked by relief workers.

Near the close of the work, after all of the above-named assistance had been lost, the work was finished through the efforts of A. L. Lewis and L. M. Martin. To all of those mentioned the author is indebted for the assistance they rendered.

WASHINGTON, February 27, 1936.

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STUDIES ON THE QUATERNARY SYSTEM CaO-MgO-$2CaO.SiO_2$-$5CaO.3Al_2O_3$

BY H. F. McMURDIE AND HERBERT INSLEY

ABSTRACT

Determinations of primary phase volumes in the system CaO-MgO-$2CaO.SiO_2$-$5CaO.3Al_2O_3$ have been made. It was found that no ternary or quaternary compounds exist and that there is no detectable solid solution among any of the compounds present. A graphic illustration is shown of the amount of MgO necessary in mixtures of CaO, $2CaO.SiO_2$, and $5CaO.3Al_2O_3$ to make MgO the primary phase. This work is a necessary preliminary step in determining the effect of the state of the magnesia in portland cement.

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I. INTRODUCTION

Portland cement clinker consists essentially of lime, alumina, silica, ferric oxide, and magnesia. The last two may be generally considered as occurring incidentally, as impurities in the basic raw materials. Both serve as fluxes to lower the temperature of liquid formation, or to increase the amount of liquid formed at a given temperature, and as such are of value in manufacture. In addition, ferric oxide may confer valuable properties on the cement, which need not be considered here, and it is frequently added deliberately to the raw materials of some special purpose cements. Beyond its effect as a flux, however, magnesia has no advantageous properties and, when present in large amounts, is definitely known to be harmful. It frequently produces excessive expansion and loss of strength in concrete after one or more years. The percentage of magnesia above which it is harmful is not known precisely. Although cements which showed no unsoundness have been made containing as much as 9.5 percent of MgO[1], the weight of evidence of tests on cements is such that practically all of the specifications used in this country limit MgO to 5 percent. The discrepancy in soundness tests on different cements containing approximately the same amounts of MgO appears to be due in part to the state in which the MgO exists in the cement.[2] In some cases MgO is known to occur

[1] P. H. Bates. Tech. Pap. BS. 10, (1918) T102.
[2] Wm. Lerch. Portland Cement Association Fellowship (Unpublished data).

as periclase (MgO), whereas, if glass occurs because of failure to attain complete equilibrium during cooling of the clinker, at least a part of the MgO must be present in the glass.

It would evidently be of considerable help in the determination of the behavior of magnesia in portland cement to establish the composition ranges within which MgO appears as a primary phase (the first phase to crystallize on cooling), but this would require the determination of a part of the equilibrium diagram of the system CaO-MgO-Al_2O_3-Fe_2O_3-SiO_2. Obviously, before this can be done it is necessary to survey the systems of fewer components which comprise the boundaries of the 5-component system. The results given in this paper represent a preliminary step in this direction.

II. EXPERIMENTAL PROCEDURE

Table 1 gives the composition of the material used in this work.

TABLE 1.—*Composition of the materials used* [1]

Constituents	Silica [2]	Alumina [3]	Magnesia [4]	Calcium carbonate [5]
	Percent	*Percent*	*Percent*	*Percent*
SiO_2	99.62		0.004	
Al_2O_3	.34	99.995		
Fe_2O_3	.02	0.05		
MgO			>99.8	
H_2O (soluble)			.15	
$CaCO_3$				99.96
$BaCO_3$				.02

[1] Water-free basis.
[2] Portland Cement Association Fellowship lot 3. Analyzed by H. C. Stecker.
[3] Baker lot 11,528. Analyzed by W. C. Taylor.
[4] Baker lot 9,132. Analyzed by Chemistry Division, National Bureau of Standards.
[5] Good lot 1,240. Analyzed by Chemistry Division, National Bureau of Standards.

Since the magnesia and alumina contain fairly large and variable amounts of water, the ignition losses were determined on the same day the mixtures were prepared. In weighing out the mixes the amount of alumina was corrected for the Al_2O_3 contained in the silica. The lime, silica, and alumina were mixed by shaking dry in a bottle, grinding in a mortar, and heating at a temperature of about 1,200° C. They were then reground, reheated at a temperature high enough to give some sintering, and then again ground. The required amounts of MgO were then added and the mixture again mixed, heated, and ground.

In some cases new mixes were made by grinding together equal amounts of two previously prepared mixes.

The quench method was used throughout. This method has been described by many investigators in high-temperature research so thoroughly as to make it unnecessary to go into details.[3]

In this work the determination of the primary phase volume of MgO and the compositions and temperatures of invariant points were the main considerations. Less attention, therefore, was paid to liquidus temperatures of compositions which were distant from invariant points.

[3] G. W. Morey. J. Wash. Acad. Sci. 13, 326 (1923); Shepard, Rankin, and Wright. Am. J. Sci. [IV] 28, 293 (1909).

The electric furnace used was wound with 80-percent platinum—20-percent rhodium wire on a 1-inch alundum tube, and the temperature control was very like that described by Roberts.[4] The charges were held at the required temperature for 20 to 30 minutes. A differential heating curve was used to check the temperature of the quaternary eutectic. Thermocouples were standardized at frequent intervals by quenching samples of diopside, $CaMgSi_2O_6$ (mp = 1,391.5° C) and calcium metaborate (mp = 1,154.5° C) from their melting temperatures.

In this work, as in others in this field, a short system of notations is used in referring to the compounds as follows:

$2CaO.SiO_2 = C_2S$	$3CaO.Al_2O_3 = C_3A$
$3CaO.SiO_2 = C_3S$	$5CaO.3Al_2O_3 = C_5A_3$

Just as a ternary system is represented on a triangle with one component at each apex, so a quaternary system is best shown on a tetrahedron with one component at each apex. While in a ternary system the liquidus temperature can be shown on a curved surface a definite height above the base, this is not possible in a quaternary system. Thus, no space representation of temperature can be made. For a discussion of the tetrahedral representation of such a system reference is made to Lea and Parker [5] and to McCaffery and coworkers.[6]

Just as the three binary systems must be known before a ternary system can be worked out, so here the four ternary systems involved must be known. These have been published [7 8 9 10] and no attempt was made to recheck their data.

This left only an exploration of the interior of the tetrahedron. This was done by making a series of mixes containing 5 percent of MgO and determining the primary-phase volumes intersected on this plane through the tetrahedron. Then a few mixtures were made with larger amounts of magnesia to determine the amount necessary to make it the primary phase. From this work the invariant points were located tentatively and these were then more closely established by means of additional mixtures.

III. RESULTS

The composition at the invariant point at which CaO, C_2S, C_3S, and MgO are in equilibrium with a liquid and vapor could only be estimated because of the high temperatures at that region. It was estimated from the other data.

Table 2 gives the composition of the mixes and results of the quenches.

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TABLE 2.—*Composition and results of quench mixes*

Mix	Composition (in percent)				Temperature, ± 5° C	Phases present
	MgO	SiO_2	Al_2O_3	CaO		
					°C	
A5	5.0	8.2	31.4	55.4	1,440	Glass only.
					1,430	Glass + CaO.
					1,420	Glass + CaO + C_2S.
					1,390	Glass + C_2S + C_3A.
B5	5.0	7.1	31.1	56.8	1,425	Glass + CaO.
					1,415	Glass + CaO + C_2S.
C5	5.0	9.0	29.5	56.5	1,503	Glass only.
					1,500	Glass + CaO.
					1,480	Glass + CaO + C_2S.
D5	5.0	8.0	29.5	57.5	1,450	Glass + CaO.
					1,400	Glass + CaO + C_2S.
E5	5.0	12.1	27.2	55.7	1,535	Glass only.
					1,525	Glass + C_2S.
					1,450	Glass + C_2S + C_3S.
F5	5.0	10.3	29.8	54.9	1,450	Glass + C_2S.
					1,400	Glass + C_2S + C_3S.
G5	5.0	8.6	32.3	54.1	1,410	Glass only.
					1,400	Glass + C_2S.
					1,375	Glass + C_2S + C_3A.
H5	5.0	6.9	34.7	53.4	1,375	Glass + C_3A.
					1,360	Glass + C_3A + C_2S.
J5	5.0	9.8	29.6	55.6	1,480	Glass only.
					1,475	Glass + C_3S.
K5	5.0	7.7	33.6	53.7	1,385	Glass only.
					1,375	Glass + C_3S.
					1,410	Glass + C_3S.
L5	5.0	8.4	31.8	54.8	1,390	Glass + C_3S.
					1,380	Glass + C_3S + C_2S + C_3A.
M5	5.0	7.4	33.4	54.2	1,400	Glass + very small amount C_2S.
					1,395	Glass + C_2S + C_3A.
N5	5.0	6.6	38.5	49.9	1,350	Glass only.
					1,340	Glass + C_3A.
O5	5.0	6.6	37.2	51.2	1,370	Glass only.
					1,360	Glass + C_3A.
Q5	5.0	5.8	39.8	49.4	1,340	Glass only.
					1,330	Glass + C_3A + MgO.
R5	5.0	6.5	39.5	49.0	1,310	Glass only.
					1,305	Glass + C_3A + C_2S + MgO.
S5	5.0	7.5	36.9	50.6	1,360	Glass only.
					1,350	Glass + C_3A.
T5	5.0	6.0	40.8	48.2	1,310	Glass only.
					1,305	Glass + C_3A + C_5A_3.
					1,300	Glass + C_3A + C_5A_3 + MgO.
G8	8.0	8.4	31.3	52.3	1,400	Glass + MgO.
G6.5	6.5	8.5	31.8	53.2	1,400	Glass + MgO.
					1,360	Glass + MgO + C_2S + C_3S.
G5.75	5.75	8.6	32.1	53.55	1,390	Glass + MgO.
					1,380	Glass + MgO + C_2S + C_3S.
E10	10.0	11.4	25.8	52.8	1,500	Glass + MgO + C_2S.
E7.5	7.5	11.7	26.5	54.3	1,500	Glass + MgO.
E6.25	6.25	11.9	26.9	54.95	1,490	Glass only.
					1,480	Glass + C_2S.
					1,440	Glass + C_2S.
					1,430	Glass + C_2S + MgO.
					1,420	Glass + C_2S + MgO + C_3S.
U5.5	5.5	7.1	33.6	53.8	1,400	Glass only.
					1,395	Glass + C_3A + MgO + CaO.
					1,390	Glass + C_3A + MgO + C_2S.
V5.4	5.4	7.8	33.9	52.9	1,385	Glass only.
					1,380	Glass + C_3A + MgO + C_2S.
					1,375	Glass + C_3A + MgO + C_2S.

Figure 1 shows a perspective three-dimensional drawing of the quaternary system CaO-C_2S-C_5A_3-MgO. The C_2S apex lies beyond the plane of the paper. In this tetrahedron the various primary-phase boundaries are indicated. The surface intersecting the sides of the tetrahedron at A, B, C, D, E, F, and G indicates the lower level of the primary-phase volume of MgO. Thus, in all mixtures with a greater percentage of MgO than represented by this surface, MgO is the primary phase. The surface extends from 33 percent of MgO on the CaO-MgO edge to slightly under 5 percent of MgO at the quater-

nary eutectic. The lines on this surface are quintuple lines. Here five phases are in equilibrium; three solid phases, one of which is MgO, and a liquid and vapor. The dotted lines lie on the base of the tetrahedron and represent boundary curves in the ternary system CaO-C_2S-C_5A_3. Surfaces connecting these two sets of lines separate the primary-phase volumes of CaO, C_3S, C_3A, C_2S, and C_5A_3.

It is seen that by far the greater part of the tetrahedron lies above the lower boundary surface of magnesia. This surface is shown in figure 2 as projected on the CaO-C_2S-C_5A_3 base, the eye being placed at the MgO apex. The full lines indicate the quintuple lines on this surface and the contours show the level of the surface in percentage of MgO. The contours are based to a large degree on the previously determined points on the ternary systems. The course of the con-

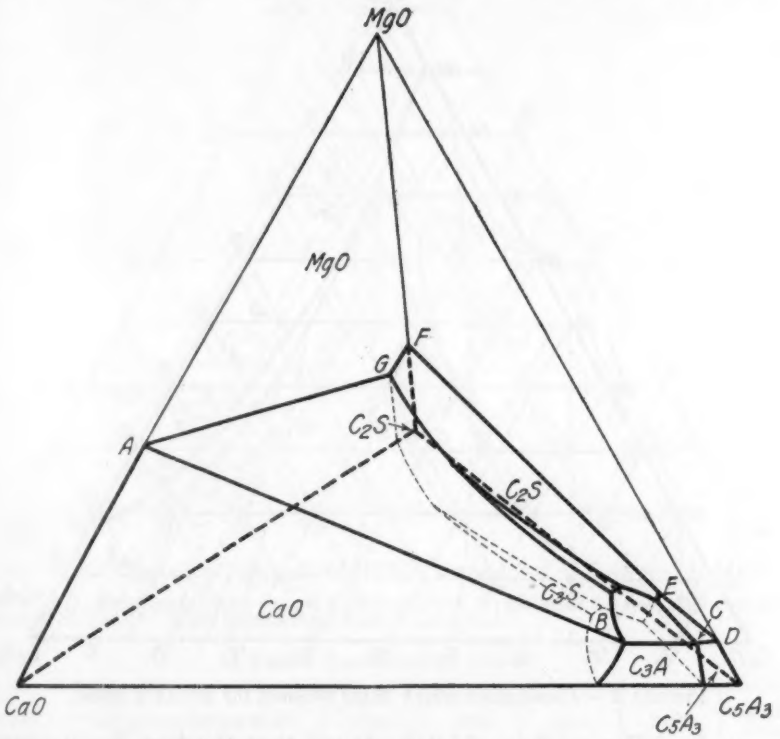

FIGURE 1.—*Quaternary system* CaO-MgO-2CaO.SiO_2-5CaO.$3Al_2O_3$.

tours below 10 percent is obtained from points determined near the invariant points U and V. The contour of 15 percent and those higher were largely interpolated by using the points on the sides of the tetrahedron. They were then made roughly parallel to contour lines representing lower percentages of magnesia. The relative amounts of CaC, C_2S, and C_5A_3 are shown by the triangular coordinates. These three components are thus shown on a basis of 100 percent. Therefore, a true percentage of CaO, C_2S, or C_5A_3 in a mixture on this surface is obtained by reducing the amount read from the coordinates by an amount proportional to the MgO percentage (read from the contours). The arrows on the lines indicate falling temperatures.

All the invariant points of the quaternary system lie on this surface. Thus the composition of the first liquid formed on heating any mixture of the four components will lie on this surface. The invariant points U and V are not eutectics, since they lie outside the tetrahedra bounded by the conjugation planes formed by joining the composition points of the four compounds at equilibrium at the respective points. Point W, however, is a eutectic.

The composition of most portland cements (if composed of CaO, Al_2O_3, SiO_2, and MgO only) would lie within a tetrahedron whose apices are the C_2S, C_3A, MgO, and C_3S composition points. Therefore, the first liquid formed on heating would be of the composition of point V and would appear at about 1,380° C. This substantiates

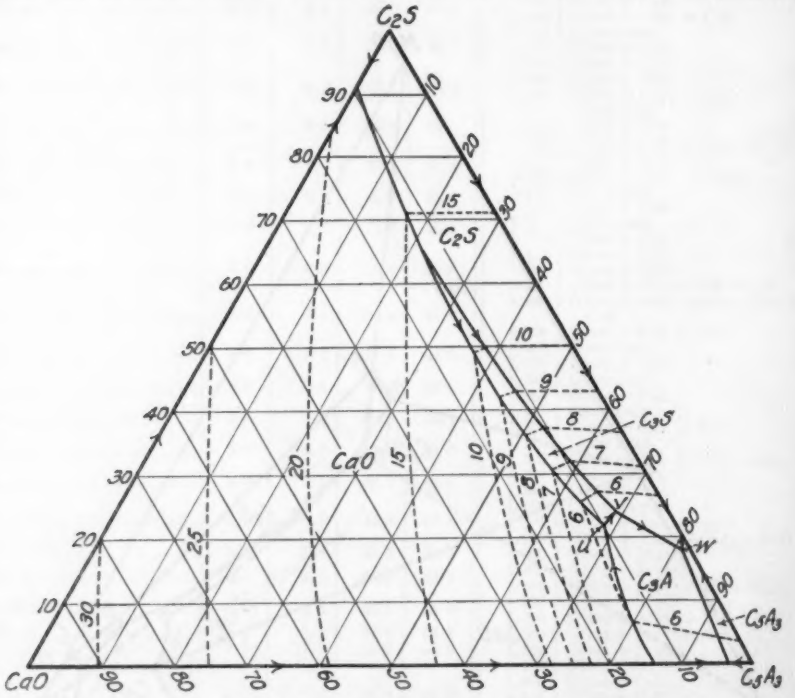

FIGURE 2.—*Plane above which* MgO *becomes the primary phase.*

the work of Hansen [11] in which he found that the first liquid formed on heating a portland cement mixture free from Fe_2O_3 appeared at 1,375° C. On further heating he found the invariant point corresponding to U to be at 1,395° C.

Figure 3 indicates the effect on the boundary curves of the addition of 5 percent of magnesia. The dotted lines are the boundary curves in the CaO–C_2S–C_5A_3 system, while the full lines indicate the position of the corresponding lines in a plane through the tetrahedron at 5 percent of MgO. The points show the location of mixes used, the compositions of which were on this plane. It must be remembered

[11] W. C. Hansen, B.S. J. Research 4, 55 (1930) RP132.

that these dotted lines do not represent a ternary system, and that as soon as a compound crystallizes from a cooling liquid whose composition lies on this plane, the composition of the liquid changes in such a way that it is no longer on this level.

The binary and ternary invariant points in the tetrahedron as obtained from the aforementioned works are shown in table 3.

Table 4 is a summary of the invariant points located in the quaternary system.

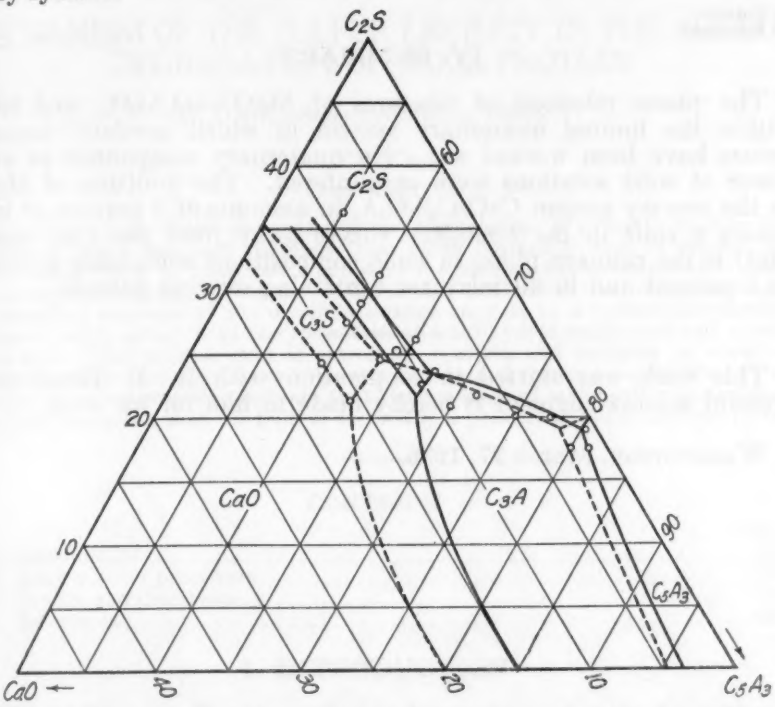

FIGURE 3.—CaO–2CaO.SiO_2–5CaO.3Al_2O_3 *as modified by 5 percent of* MgO.

Dotted lines show original boundary curves from Rankin and Wright, while full lines show boundaries with 5% of MgO added. Points indicate composition of quench mixes.

TABLE 3.—*Invariant points*

Liquid and vapor in equilibrium with—	MgO	SiO_2	Al_2O_3	CaO	Temperature
Binary:	*Percent*	*Percent*	*Percent*	*Percent*	°C
CaO-MgO[1]	33			67	2,300
C_2S-MgO[1]	20	28		52	1,925
C_3A_3-MgO[1]	6.5		44.5	49	1,832
C_2S-CaO[1]		32.5		67.5	2,065
C_2S-C_3A_3[1]		7.0	42.0	51.0	1,350
C_3A_3-C_3A[1]			50	50	1,395
C_3A-CaO			41	59	1,535
Ternary:					
CaO-C_2S-MgO[1]	19	23		58	1,990
C_2S-C_3A_3-MgO[1]	5	6.5	39.5	49	1,315
C_3A_3-C_3A-MgO[1]	6.3		47.7	46	1,345
CaO-C_2S-C_3S		22.4	9.2	68.4	1,900
CaO-C_2S-C_3A		7.5	32.8	59.7	1,470
C_2S-C_3A-C_3S		8.7	33.0	58.3	1,450
C_2S-C_3A-C_3A_3[1]		6.8	41.2	52.0	1,335
CaO-C_3A-MgO	6.2		42.3	51.5	1,452

[1] Eutectic.

TABLE 4.—*Quaternary invariant points*

Liquid and vapor in equilibrium with—	MgO	SiO_2	Al_2O_3	CaO	Temperature
	Percent	*Percent*	*Percent*	*Percent*	°C
CaO-C_3S-C_3A-MgO	5.5	7.0	33.5	54.0	1,395±5
C_3S-C_2S-C_3A-MgO	5.5	7.5	34.0	53.0	1,380±5
CaO-C_2S-C_3S-MgO	[b] 14.0	[b] 19.0	[b] 10.0	[b] 57.0	
C_3A-C_3A_3-C_2S-MgO [a]	5.0	5.0	41.5	48.5	1,295±5

[a] Eutectic.
[b] Estimated.

IV. SUMMARY

The phase relations of mixtures of MgO,CaO,Al_2O_3, and SiO_2 within the limited quaternary system in which portland cement occurs have been worked out. No quaternary compounds or evidence of solid solutions were encountered. The addition of MgO to the ternary system CaO-C_2S-C_5A_3 in amounts of 5 percent or less causes a shift in the boundary curves away from the CaO apex. MgO is the primary phase in some compositions containing as little as 5 percent and in all mixtures containing over 33 percent.

This work was started in cooperation with R. H. Ewell, and grateful acknowledgment is hereby made to him for his work.

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MECHANISM OF THE SULFUR LABILITY IN THE ALKALI DEGRADATION OF WOOL PROTEIN

By J. A. Crowder and Milton Harris [1]

ABSTRACT

It is the purpose of this paper to describe the behavior of sulfur in wool under conditions which are very different from those ordinarily used in studies on sulfur lability and to point out a probable mechanism by which sulfur is split from wool during alkali treatment. The data indicate that the primary process in the alkali cleavage of the disulfide linkage consists in a hydrolytic rupture of the disulfide group with the formation of a sulfhydryl compound and a sulfenic acid. The sulfenic acid is extremely reactive and unstable in alkaline solution and immediately loses hydrogen sulfide and forms an aldehyde. The results of the investigation indicate that the existence of labile sulfur in proteins is not an indication that the bulk of the sulfur is present in more than one form.

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I. INTRODUCTION

The lability of sulfur in cystine and cysteine and their derivatives, and in various disulfides, mercaptans, and proteins has recently received much attention. Excellent reviews and bibliographies on the voluminous literature on this subject are recorded in the papers of Gortner [1] [2] and Clarke [2] and their collaborators and for that reason need not be discussed here.

Labile sulfur is an arbitrary name given to that portion of the sulfur which splits off from sulfur-containing substances on treatment with various alkalies or with alkaline solutions of various reagents such as lead acetate, lead nitrate, etc. It is obvious that the value obtained for the amount of labile sulfur will depend on the method used and the specific conditions of treatment. There have been postulated several mechanisms, which will be discussed later, for the splitting of sulfur from cysteine, cystine, and other mercaptans and disulfides. In the case of proteins, however, results which have appeared to be anomalous have led a number of in-

[1] Research Associates at the National Bureau of Standards, representing the American Association of Textile Chemists and Colorists.

[2] The numbers in brackets here and throughout the text refer to the references at the end of this paper.

vestigators [3] to assume the existence of a number of sulfur combinations in proteins.

The results of the present investigation make it unnecessary to assume that the existence of labile sulfur in proteins is an indication that the bulk of the sulfur is present in more than one form. It is the purpose of this paper to describe the behavior of sulfur in wool under conditions which are very different from those ordinarily used in studies on sulfur lability, and to point out a probable mechanism by which sulfur is split from wool during alkali treatment.

II. EXPERIMENTAL PROCEDURE

Purified wool yarn, the preparation and properties of which have been described elsewhere [4], was used in this work. The alkali treatments were performed in a 2-liter filtering flask, fitted with a dropping funnel for passing liquid into the flask and having the side-neck connected to a suction pump for removal of the liquid. The flask was immersed in a water bath at 65° C. During the treatments, every precaution was taken to keep oxygen out of the reaction mixture. A 6-g sample of wool was placed in the suction flask and the air exhausted and replaced with nitrogen. 600 ml of a 0.05*N* solution of sodium hydroxide, previously boiled to remove dissolved air, was then added. The flask was shaken frequently. At the end of each treatment, the supernatant liquor was drawn off and the wool washed by running freshly distilled water through the flask until the washings were no longer alkaline to phenolphthalein. The water remaining in the flask was drawn off and the wool was partially dried under reduced pressure at 65° C for two hours. The wool was then rapidly transferred to a vacuum desiccator, where it was dried to constant weight over calcium chloride. After drying, all samples were stored in an atmosphere of nitrogen.

III. RESULTS AND DISCUSSION

Samples of purified wool were treated as previously described for varying periods of time. The loss in weight of the wool and the sulfur and cystine content of the alkali-treated wool are given in

TABLE 1.—*Effect on wool of the continued action of 0.05N solution of sodium hydroxide at 65° C*

Time of treatment	Loss in weight	Alkali-treated wool	
		Sulfur content	Cystine content, by Sullivan method
Minutes:	*Percent*	*Percent*	*Percent*
0	0	3.72	13.40
15	2.27	2.91	6.91
30	3.52	2.56	4.85
45	4.67	2.35	5.13
Hours:			
2	6.4	2.24	4.41
4	9.38	2.13	3.70
8	15.21	2.03	2.64
46 [a]	61.50	2.28	2.65

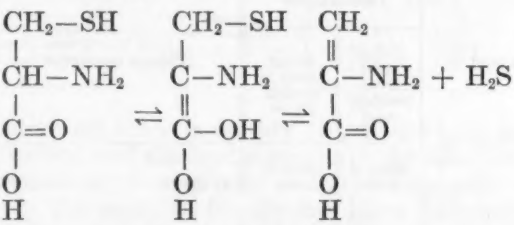
[a] The samples became gelatinous and part of the residual wool was lost during washing. The accuracy of these values are questionable.

table 1. The results [3] are in good agreement with those obtained previously [4] although no precautions were taken to exclude oxygen in the earlier experiments.

The data indicate a rapid splitting off of a portion of the sulfur during the early stages of the treatment. After about four hours the sulfur content approaches a constant value, which is not significantly changed on further treatment.

The conditions under which these experiments were carried out, namely, the temperature and concentration of the alkaline solutions and the duration of treatment, are very mild compared with those generally used in determining the labile sulfur in cystine, cysteine, or their derivatives. The extreme ease with which approximately one-half of the sulfur is removed from wool under such comparatively mild conditions suggests that the first step in the alkali degradation of wool is a splitting of the disulfide linkage into one labile and one comparatively stable sulfur group.

Two mechanisms for the sulfur lability in cysteine and its derivatives and in disulfides have been recently advanced by Nicolet [5] and by Schöberl and Wierner [6]. The former suggests that the removal of sulfur from cysteine by alkalies takes place as a 1,4-elimination of hydrogen sulfide from an intermediate enolized form according to the following equations:



(1)

He also suggests that from cystine, RSSH or eventually H_2S_2, would split out.

Schöberl and Wierner studied the alkaline cleavage of disulfides and found evidence that the primary process in the cleavage of aliphatic disulfides of a definite type consisted in a hydrolytic rupture of the disulfide linkage with the formation of a sulfydryl compound and a sulfenic acid according to the following scheme:

$$R{-}CH_2{-}S{-}S{-}CH_2R \longrightarrow RCH_2SH + HOSCH_2R \qquad (2)$$

The sulfenic acid, being extremely reactive and unstable in alkaline solution, immediately loses H_2S and forms an aldehyde according to equation 3.

$$RCH_2{-}SOH \longrightarrow RCHO + H_2S \qquad (3)$$

They also postulate that in the presence of air, the sulfhydryl groups will be reoxidized to disulfide groups, after which the reaction in equation 2 would again take place. Even though air were not excluded during the alkali treatment of wool, it would be very doubtful whether such a reaction might take place, since the sulfhydryl groups are held in fixed positions in the wool molecule and would thus be kept from recombining.

[3] In comparing the values obtained in the present work with those in the earlier experiments, it should be noted that the data in this paper are calculated on a dry-wool basis, while those in the previous experiments were based on the weight of the conditioned wool.

The experimental evidence in the present investigation indicates that the alkali degradation of wool proceeds according to equations 2 and 3. When the alkali-treated samples were tested for aldehydic properties with Schiff's reagent, it was found that an intense violet-red color was formed on the wool in a few seconds, while the untreated wool was colored only a faint pink by the same treatment. Similarly the alkali-treated samples gave positive sulfhydryl reactions with ammoniacal sodium nitroprusside solutions, while tests on the untreated wool were negative. It can also be easily demonstrated that the sulfur which is split off from the wool is in the form of inorganic sulfides. If an aliquot of the mother liquor from the alkali treatment is saturated with bromine and heated on a steam bath for one-half hour, the sulfur is oxidized to sulfate and can be determined as barium sulfate. It has been shown that the sulfur in wool or in cystine is not oxidized to sulfate under these conditions. The losses in sulfur of the wool, calculated from the sulfur contents of the alkali-treated samples and also from the sulfur found in the mother liquor are given in table 2.

TABLE 2.—*Loss of sulfur from wool resulting from the continued action of 0.065N solutions of sodium hydroxide at 65° C*

Time of treatment	Loss in sulfur		Time of treatment	Loss in sulfur	
	Calculated from residual wool	Sulfur found in mother liquor		Calculated from residual wool	Sulfur found in mother liquor
Minutes:	mg/g of wool	mg/g of wool	*Hours:*	mg/g of wool	mg/g of wool
10	4.4	4.0	1	11.6	11.3
20	8.8	7.4	2	12.8	12.1
30	10.1	9.7	3	14.0	13.6
40	10.4	9.8	4	14.5	14.0
50	10.9	10.2	5	14.9	14.8

It has been previously mentioned that under the conditions of these experiments, cysteine and its derivatives would be comparatively stable. That the sulfur in the cysteine in wool (obtained by reducing wool in alkaline solution) is stable under these conditions is readily shown by treating wool with 0.05*N* solution of sodium hydroxide containing 1 percent of sodium sulfide. After 2 hours' treatment the wool loses about 5 percent of its sulfur, whereas in the same treatment with no sodium sulfide present wool loses about 40 percent of its sulfur.

It is apparent that since the wool is not in solution, not all of the disulfide groups will react with alkali simultaneously. It is probable, therefore, that sodium sulfide, which is immediately formed by the action of the sodium hydroxide on some of the disulfide groups, will tend to reduce unreacted disulfide groups to sulfhydryl groups and make them more stable towards the alkali. On the basis of this, it follows that if the sodium sulfide is removed from contact with wool as rapidly as possible, the sulfur content of the residual wool should be lower than that of wool which is allowed to remain in contact with the sodium sulfide. In order to test this 5- and 12-g samples of

wool were placed in 400-ml flasks and a 0.05*N* solution of sodium hydroxide at 65° C was allowed to flow continuously into the flasks so that the wool was in practically constant contact with fresh alkali. After 4 hours' treatment, the samples were washed and dried as previously described and analyzed for loss in weight and sulfur and cystine contents. The results are recorded in table 3 and are compared with results obtained on a regular 4-hour sample (table 1). The data constitute further evidence that the labile sulfur comes from the formation of a sulfur compound other than cysteine and that cysteine is relatively stable under the conditions of these experiments. It is also of interest to note that in treatment (4), table 3, the 50 percent splitting off of sulfur that would be expected under ideal conditions is closely approached.

TABLE 3.—*Comparison of the effect on wool of standing and flowing baths of 0.05N solutions of sodium hydroxide at 65° C*

[Time of treatment 4 hours]

Treatment	Loss in weight	Sulfur content	Fraction of total sulfur lost	Cystine content
	Percent	*Percent*	*Percent*	*Percent*
(1) None		3.72		13.4
(2) Regular standing bath (from table 1)	9.4	2.13	42.7	3.7
(3) 25 liters of alkali flowed over 12 g of wool	14.4	2.02	45.7	2.6
(4) 45 liters of alkali flowed over 5 g of wool	14.3	1.92	48.4	2.5

While qualitative evidence is readily obtained which indicates the presence of sulfhydryl and aldehydic groups in the alkali-treated wool, tests for the presence of those groups in the hydrochloric acid hydrolysate obtained in the analysis for cystine were definitely negative. However, when the reactivity of the aldehydic and sulfhydryl groups formed in the hydrolysate is considered, it is not surprising that negative tests were obtained. Under the conditions of the hydrolysis, namely, 6*N* hydrochloric acid at 120° C for 9 hours, it is very probable that recombination between the aldehydic and sulfhydryl groups may take place. A suggested mechanism for such a reaction would be the formation of a thioacetal. To test for the formation of stable thio-compounds, hydrolysis was carried out in 18*N* sulfuric acid. Acid of this strength is known to cleave thio-compounds which are stable to more dilute acids. The results in table 4 show that the values obtained by use of 18*N* sulfuric acid are definitely higher than the values obtained with 6*N* acid. The somewhat higher values for cystine obtained by the Folin-Marenzi method are in accord with results obtained by other investigators and may be attributed to lack of specificity of the Folin-Marenzi reagent. It may be concluded, however, that a more stable thio-compound is formed in the dilute acid hydrolysate.[4]

[4] There is also a possibility that some of the sulfhydryl formed in the wool during the alkaline treatment may react to form a stable thio-compound even before hydrolysis. Further investigations are now in progress.

TABLE 4.—*Cystine analysis of alkali-treated wool using 6N and 18N sulfuric acid for the hydrolysis*

Time of treatment	Sulfur content	Cystine content, Sullivan method		Increase in cystine content	Cystine content, Folin-Marenzi method		Increase in cystine content
		$6N$ H_2SO_4	$18N$ H_2SO_4		$6N$ H_2SO_4	$18N$ H_2SO_4	
Hours	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
0	3.72	13.3	13.0	−2	13.2	13.0	−2
4 [a]	2.02	2.2	3.1	+41	3.6	4.6	+28
8	2.03	2.6	3.5	+35	2.9	3.6	+24

[a] Sample 3 (table 3), which was treated with flowing alkali solution.

The work was made possible, in part, by a grant from The Chemical Foundation, and we wish to express our appreciation for the aid.

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WASHINGTON, February 21, 1936.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP886

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A MODIFIED ACCELERATED WEATHERING TEST FOR ASPHALTS AND OTHER MATERIALS

By O. G. Strieter[1] and H. R. Snoke

ABSTRACT

A modified method for testing asphalts and similar complex materials by accelerated weathering is described.

A variety of materials are shown to exhibit the same type of chemical changes when exposed to the accelerated weathering cycle. The experiments show that the weathering process gradually transforms these materials into products that are largely soluble in water, and that these soluble products may be collected quantitatively for examination and identification. The function of light and oxygen in the weathering process is explained, and data are given to show that the products of accelerated weathering are similar to those obtained in outdoor exposures. New applications of accelerated weathering are suggested.

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I. INTRODUCTION

The weathering of asphalts has been studied by a number of investigators, and the fact that exposure to sunlight renders asphalts insoluble in certain organic solvents is well established, having at one time been extensively used in photography.[2] That the products formed by the weathering of asphalts are largely soluble in water is not widely known [3] and has not been previously investigated.

It has been shown in a previous paper [4] that asphalts behave similarly when exposed to accelerated and to outdoor weathering. However, in previous tests conclusions were drawn only from the appearance of the weathered asphalt, since no provision was made to recover any of the products of weathering.

[1] Research Associate at the National Bureau of Standards, representing the Asphalt Shingle and Roofing Institute.

[2] Herbert Abraham, Asphalts and Allied Substances, 3d ed., p. 835 (D. Van Nostrand Co., New York, 1929).

[3] See p. 838 of reference 2.

[4] O. G. Strieter, BS J. Research 5, 247 (1930) RP197.

II. WEATHERING OF ASPHALTS AND OTHER MATERIALS

For the purpose of this investigation, the following types of materials were selected: asphalt A, of softening point 220° F; asphalt B, of softening point 160° F; and C, asphalt-saturated felt and smooth-surfaced asphalt-prepared roofing.

Material A was surfaced on aluminum plates to a thickness of 0.025 inch and subjected to a cycle consisting in 19 hours exposure to light and heat from a carbon-arc lamp and 5 hours immersion in distilled water, at room temperature, until the water was colored a decided brown. Material B was an asphalt that had been exposed outdoors in a location of abundant sunlight, relatively high humidity, and practically no rainfall; and material C had been exposed outdoors at the National Bureau of Standards for a period of 7 years.

Materials B and C were immersed in water and the solutions filtered to remove any suspended matter. These solutions, and that obtained from material A, were evaporated to dryness and the residues dried at 105° C. These residues were quite similar in appearance, being resin-like and brittle, black in color (brown when pulverized or in thin layers), and with an odor resembling caramel or burnt sugar.

Each of these products was found to be acid and to reduce Fehling's solution. The most concentrated solution which could be read with a polariscope was 200 mg of substance in 10 ml of water in a tube 20 mm long. No rotation could be detected. The acidity was determined by titration with $N/10$ alkali, using litmus as indicator. The acidity is expressed (table 1) as milliliters of $N/10$ alkali necessary to neutralize 1 g of water-soluble substance. The reducing power was determined quantitatively by the method of Allihn and the values given in table 1 represent the reducing power expressed as dextrose.

TABLE 1.—*Reducing power and acidity of water-soluble material*

Material	Method of exposure	Reducing power in terms of dextrose	Acidity $N/10$ alkali
		%	ml/g
A	Accelerated cycle	8	37
B	Outdoors	9	9
C	Outdoors	10	15

The reducing substance was found to be precipitated by the addition of an excess of basic lead acetate solution. The excess of lead in the clear filtrate from this solution was precipitated with a minimum amount of ammonium oxalate and this filtrate produced only a very slight reduction of Fehling's solution. The basic lead precipitate obtained above was then decomposed by hydrogen sulphide and the aerated filtrate was found to reduce Fehling's solution strongly. Such behavior points to the presence of ketone acids in the water-soluble material.

The authors are indebted to D. H. Brauns of the Polarimetry Section at the National Bureau of Standards for the examination of the asphaltic residues described above.

A sample of asphalt (approximately 6 g), surfaced on an aluminum panel to a thickness of 0.025 inch and alternately exposed to light from the carbon-arc lamp and immersed in water for 24-hour periods, showed a loss in weight of 0.2070 g after 668 hours of light exposure. The water in which the asphalt was immersed yielded 0.1910 g of residue. The fact that the loss in weight of the asphalt is nearly the same as the amount of water-soluble product recovered is not necessarily significant.

Bleached cotton cloth, wool cloth, and rubber (in sheet form) were also treated by alternate exposure to light and heat from the carbon-arc lamp and immersion in distilled water, the cotton and wool cloths being treated before exposure with organic solvents to remove waxes. Resin-like substances which were brittle, acid to litmus, and had a caramel odor were obtained by evaporating these water solutions. They were somewhat lighter in color than those obtained from the asphaltic materials, and, except that obtained from the wool cloth, reduced Fehling's solution.

The extent to which these materials are converted into water-soluble products by the accelerated weathering action has not been determined. However, from the observations thus far made there is no indication that the rate of weathering decreases with time or that the nature of the reactions involved in weathering changes. While the solutions in which the test specimens are immersed are uniformly clear, it is apparent that small quantities of unweathered material are present, so that the residues obtained by evaporating the solutions may not completely redissolve after drying.

III. THE FUNCTION OF LIGHT AND OXYGEN IN WEATHERING

To determine the function of light and oxygen in the weathering of asphalts the following experiments were devised. Asphalt (softening point 105° C) was placed in two U-tubes with 5 ml of freshly boiled distilled water in each. The asphalt was spread over approximately half of the inside surface of each neck of the tubes and was kept far enough from the bottom that it was not in contact with the water. In one tube the air was replaced with oxygen and in the other with carbon dioxide. The tubes were tightly stoppered and exposed to light from the carbon-arc lamp, being so arranged that light from the lamp passed through the uncovered sections of the tubes to the exposed asphalt surfaces. After light periods totaling 25 hours, moisture condensed in small droplets on the cooled surface of the asphalt exposed to oxygen. On washing the asphalt surface, the water was colored slightly yellow. The other tube, exposed and treated exactly as the one above, showed no droplets condensed on the surface of the asphalt and no color in the water. These exposures were continued for 370 hours, the tubes being cooled to room temperature and the surfaces of the asphalts washed with the water in the tubes once each day. At the end of this period the surface of the asphalt exposed to oxygen was dulled and covered with minute hair cracks or checks, and was readily wetted by the water, which was colored a decided yellow. The surface of the asphalt exposed to carbon dioxide was also dulled, but to a lesser extent, and showed surface lines in irregular patterns. The surface was not wetted

when washed with the water, the water was not discolored, and droplets were not condensed on the surface of the asphalt on cooling. The water was taken from the tubes at the end of this exposure, the tubes thoroughly washed with distilled water, and the original water and washings combined and evaporated to dryness, dried in an oven at 105° C for two hours and weighed, giving residues as follows:

Tube containing oxygen	0.0250 g.
Tube containing carbon dioxide	0.0015 g.

A similar tube was prepared with the same asphalt and an atmosphere of oxygen, and exposed for 370 hours at a temperature of 80° C in the dark. After 24 hours droplets condensed on the surface of the asphalt on cooling, but at the end of the exposure the surface of the asphalt was slightly dulled. The dried residue obtained from this water weighed 0.0023 g.

These experiments show that both light and oxygen are necessary for the production of water-soluble products. Other investigators [5] found that oxygen was necessary in the presence of light to form products insoluble in benzene, chloroform, and similar solvents, but thought that the oxygen acted as a catalyst in the formation of more complex compounds insoluble in organic solvents. However, these observations show that oxidation products soluble in water are formed.

IV. THE MODIFIED ACCELERATED WEATHERING CYCLE

The accelerated weathering test for asphalts mentioned above (section II, footnote 4) consists in exposing the material under test alternately to light and heat from a carbon-arc lamp, a period of refrigeration, and a period during which water is forcefully sprayed on the surfaces that have been exposed to the light. In this modified test, immersion in distilled water, at room temperature, for a period of 4 to 5 hours, is substituted for the water spray, and the refrigeration period is omitted. The progress of weathering may be followed quantitatively by evaporating the water solution at regular intervals (after 10 or 15 cycles), and drying and weighing the residue.

V. APPLICATIONS OF THE MODIFIED ACCELERATED WEATHERING CYCLE

It is not expected that this modified accelerated weathering cycle will replace the previous cycle which has been adopted as a standard by a number of users. However, it should prove a valuable research tool in the investigation of many practical problems in which weathering is involved, for example, the effect of antioxidants in such materials as asphalt and rubber and of mineral fillers in asphalts, or in the study of the adhesion of asphalt to mineral granules, important in roofing and road work. It may be of value in studying such complex materials as asphalts, coal, rubber, cotton, starch, wood, or wool, and the changes that occur in these materials during natural deterioration.

[5] Paul Gödrich, Beiträge zur Chemie der Asphalte mit besonderer Berücksichtigung ihrer photochemischen Eigenschaften, Monatsh. Chem. **36**, 535–548 (1915), also Ueber die Ursachen des Ausbleichens der Asphaltgesteine, by Edmund Graefe, Asphalt Teer Strassenbautech. **32**, 625 (1932).

VI. SUMMARY

1. The previously described "accelerated weathering cycle" for asphalts, consisting in alternate exposure to an arc light, refrigeration, and washing with a spray, has been modified by omitting the period of refrigeration, and by dipping the specimen in water instead of spraying. The wash water is then examined for soluble organic products.

2. Chemical examination of the water-soluble products obtained by weathering asphalts showed the presence of acid and ketone groups. Cotton, rubber and wool treated in the same manner gave water-soluble products similar in appearance and odor to those from asphalt, and which were acid and, with the exception of that obtained from the wool cloth, reduced Fehling's solution.

3. Tests are described which show that the formation of the water-soluble materials from asphalt depends on exposure to light and the presence of oxygen.

4. Possible applications of accelerated weathering followed by the examination of the soluble products are suggested, including the study of the function and effectiveness of antioxidants. The examination of the soluble products of weathering may also throw light on the composition of the parent materials.

The authors express their appreciation to W. Harold Smith of the Bureau's Section of Organic Chemistry, who prepared the rubber samples for test; to E. H. Berger of the Johns-Manville Corporation, New York City, who furnished asphalt B.

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EFFECTS OF PARTIAL PREHYDRATION AND DIFFERENT CURING TEMPERATURES ON SOME OF THE PROPERTIES OF CEMENT AND CONCRETE

By F. B. Hornibrook, G. L. Kalousek, and C. H. Jumper

ABSTRACT

Data presented were obtained in studies of three types of commercial cements, including two low-heat Boulder Dam, two high-early-strength, and six standard portland cements. Portions of each of the cements of the latter two types were steam prehydrated so that the ignition losses were increased for each cement to approximately 3 and 5 percent, respectively. The heats of hydration and also the compressive strengths of concrete specimens made of the untreated and of the prehydrated cements were determined for the ages of 7, 28, 90 days, and 1 year. Three curing conditions were used; continuous storage at 70° F, continuous storage at 150° F, and three respective combinations of storage at 70 and 150° F. Chemical analyses, calculated compound compositions, and specific surfaces are given. The heats of hydration and compressive strengths were both reduced by prehydration of the cements, the 5 percent prehydration causing greater reductions than the 3-percent. At the later ages the heats of hydration obtained at continuous 150° F curing were lower than the heats obtained at continuous 70° F curing. The strengths at later ages, however, were not greatly affected by the curing temperature. The 5-percent prehydrates of standard portland cements had heats of hydration that would pass the low-heat specifications for Boulder Dam cements. The expansion results on specimens made of the untreated and of the prehydrated cements stored in sodium sulfate solutions show that with the exception of the cements high in tricalcium aluminate the prehydrations increase the resistance to the action of sodium sulfate. The 5-percent prehydrates had greater resistance to the sulfate action than the 3-percent.

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I. INTRODUCTION

General recognition has been given the importance of preventing the development of excessive temperatures within large masses of concrete caused by the heat evolved from the hydrating cement. Some of the cracking that has occurred in mass concrete undoubtedly has been caused by the expansion and contraction accompanying the excessive rise and fall of temperatures. These large temperature changes may be restricted by removing the heat with an integral cooling system, or by the use of "low-heat" cements.

The numerous studies that have been made on methods of producing low-heat cements have centered chiefly on the effects of chemical and compound composition and fineness of grinding on the heat of hydration. Scattered findings of several investigators have indicated that another method of producing a low-heat cement might be that of partially hydrating standard portland cements prior to use.

In a preliminary survey made at this Bureau of possible sources of low-heat cement for Boulder Dam, commercial cements which had been partially prehydrated were studied [1].[1] It was found that neat-cement pastes made with prehydrated cements evolved less heat up to 24 hours than pastes made from the corresponding untreated cements. S. L. Meyers [2] found that prehydration of a cement with increasing amounts of water retarded the heat evolution in increasing amounts for the first 3 days of hydration; for an addition of 3.58 percent of water the 3- and 7-day strengths were also consider-

[1] The numbers in brackets here and elsewhere in the text refer to the numbered references at the end of the paper.

ably reduced. Woods and co-workers [3], and also Davis and co-workers [4], found that cements aged in the laboratory so the loss on ignition was appreciably increased had reduced heats of hydration.

In order to obtain more comprehensive data on the effect of partial prehydration on the several properties of cement, the Bureau undertook the study of two types of cement that were prehydrated with steam at atmospheric pressure so that the total ignition loss was increased in each case to approximately 3 and 5 percent. These cements, before and after partial prehydration, are compared with Boulder Dam low-heat cements.

II. DESCRIPTION OF CEMENTS

1. TYPES OF CEMENTS USED

Three types of portland cements, consisting of 10 different commercial brands, were used in this investigation. Two of the group were high-early-strength, six were standard, and two were Boulder Dam low-heat portland cements. The low-heat cements were composites of a number of samples of Boulder Dam cements passing Bureau of Reclamation specification 591–D. Portions of two high-early-strength and six standard portland cements were prehydrated to have approximately 3 and 5 percent loss on ignition, respectively.

2. CHEMICAL ANALYSIS AND FINENESS

Complete chemical analyses and determinations of specific surface were made of all cements;[2] the results are presented in table 1. The specific surfaces, expressed in square centimeters per gram of cement, were determined with the Wagner turbidimeter [5].

TABLE 1.—*Chemical analyses and calculated compound compositions of the cements*

Cement	Chemical composition									Compound composition									
										Bogue [1]				A [3]			B [3]		
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Loss on ignition	Insoluble in HCl	Free CaO	C_3S	C_2S	C_3A	C_4AF	C_3S	C_2S	Glass	C_3S	C_2S	C_3A	C_4AF
A	26.0	2.4	3.7	63.3	1.6	1.6	1.0	0.1	0.2	27	55	6	7	27	52	16	27	55	6	7
B	23.0	5.5	5.4	58.5	4.1	1.8	1.3	.2	[5]	14	56	5	17	8	55	28	14	56	5	17
C	21.6	6.0	4.8	64.3	1.2	1.6	.9	.1	.6	50	23	3	18	42	24	27	50	23	3	18
D	21.5	3.0	5.2	62.9	4.8	1.8	1.1	.3	.5	46	27	9	9	47	22	22	47	26	8	9
E	19.7	2.4	7.6	64.1	3.3	1.8	1.1	.2	.4	50	19	16	7	57	8	28	57	13	10	7
F	20.7	[4] 2.9	6.0	63.4	3.0	2.0	1.5	.2	.4	50	22	12	7	54	14	23	56	18	8	7
G	20.5	3.0	6.2	63.5	2.8	1.6	1.8	.3	.7	49	22	12	9	52	15	25	52	20	10	9
H	21.7	2.3	5.8	65.1	2.6	1.8	1.1	.5	.1	52	23	11	7	56	15	22	56	20	7	7
I	18.8	2.5	7.0	64.3	3.3	2.4	1.2	.2	1.2	56	11	14	18	62	1	26	62	6	9	8
J	21.3	3.4	5.2	61.2	4.5	2.9	1.8	.5	[5]	39	31	8	11	39	27	23	39	31	8	11

[1] Compounds calculated according to method of Bogue.
[2] Compounds calculated according to method of Lea; "liquid forms a glass."
[3] Compounds calculated according to method of Lea; "crystallizes independently at 1,400° C."
[4] Contains 0.5% of ferrous iron.
[5] Trace.

3. PREHYDRATION

The partial hydration of the cements was obtained by exposing each cement to an atmosphere of steam in a rotating oven maintained

[2] The chemical analyses were made by E. P. Flint, and the determinations of specific surface were made by R. L. Blaine, both of this Bureau.

at about 100° C by means of electrical heaters. The charge in the oven was first brought to a temperature of 100° C, then the steam, which was generated in a flask at atmospheric pressure, was passed into the oven. Because of the heat losses through the walls of the oven, the temperature in the region near the walls was below 100° C. Under these conditions it was possible to prehydrate a cement in approximately 3 hours. There was some caking of the cements on the walls of the oven, but the product obtained was easily broken up. The charge, after removal from the oven, was crushed and passed through a 20-mesh sieve, then ground in a ball mill to the approximate fineness of the original cement. The loss on ignition was determined by the standard method.

What actually takes place during the steam hydration is not definitely known. Bied [6] found that steam treatment of "entirely silicious cements" above 100° C did not cause them to absorb water. "Artificial cements" and "quick-setting cements", however, did absorb water at 110° C. Kline and Phillips [7] found that the individual compounds of cement, when exposed to steam, hydrated at different rates. Tricalcium aluminate, at 100° C and lower temperatures, hydrated much more rapidly than tricalcium silicate, while dicalcium silicate showed no appreciable hydration for the given exposures up to 4 hours. These compounds in the pure crystalline form as studied by Kline and Phillips undoubtedly behave differently than when in a heterogeneous mixture such as cement, especially since in the cement some of the alumina may be in the glass phase [8].

Throughout this paper the two series of prehydrated cements are referred to as the 3- or 5-percent prehydrates. This designation refers to the total loss on ignition of the respective series and not to the amount of water added by the steam treatment. Inasmuch as the original ignition losses of the cements ranged from 0.9 to 1.8 percent, the actual amounts added by the prehydration treatment were correspondingly less than indicated by the 3- and 5-percent designations. No attempt was made to determine what part of the total water was actually combined chemically and what part was so-called "free water."

III. PREPARATION AND TESTING OF SPECIMENS

1. HEAT OF HYDRATION TESTS

The results for heat of hydration were obtained by the heat of solution method [3]. The value for the heat of solution of the test specimen, subtracted from the value for the heat of solution of the original sample (cement or prehydrate), gave the heat of hydration.

The results are expressed on the basis of calories per gram of the original sample of cement or prehydrate (not on the ignited weight basis).

(a) APPARATUS

The calorimeter in which the heats of solution were determined is identical with that developed by the Bureau for the routine testing of the cements used in the construction of Boulder Dam.[3] The details

[3] The Bureau calorimeter is a refinement of the general type developed by Woods and co-workers [3], that developed at the University of California [9], and that described by Stenzel and Morris [10].

of construction and operation of the calorimeter are described in U. S. Bureau of Reclamation specification 566 for Boulder Dam cement.

In brief, the calorimeter consists of an outer vessel with exit chimneys in the lid, an inner or reaction vessel, a cylindrical heating unit which also acts as a stirring tube, and a bakelite valve for introducing the cement charge. All metallic surfaces within the calorimeter exposed to acid are coated with acid-resistant enamel. A stirrer of clear bakelite propelled by a synchronous motor provides the stirring. The temperature rise is measured with a 25-ohm platinum resistance thermometer, encased in a platinum sheath, in conjunction with a Mueller temperature bridge. The acid charge for dissolving the cement sample is a mixture of 10.0 ml of cp hydrofluoric acid (48%) and 648.5 g of 2.500±.002 normal nitric acid. During a determination of heat of solution the calorimeter is immersed in a water bath which is maintained at 25.000±.005° C by automatic control. Calibration of the calorimeter and contents is effected by passing a measured amount of electric current through the heating coil of known resistance, and measuring the resultant temperature rise. The heat-capacity determinations were made in duplicate at frequent intervals, the precision of the apparatus being such that the duplicates checked within 0.1 percent.

(b) PREPARATION AND STORAGE OF SAMPLE

A smooth cement paste was prepared by intimately mixing the cement and water in a ratio of 1:0.53, by weight. The required number of glass specimen vials were filled and stoppered with corks. The vials to be stored continuously at 70° F were further sealed with paraffin; all other vials were sealed with a high-melting bituminous material. All specimens were stored at 70° F for the first 24 hours. One series of specimens, hereinafter designated as the constant 70° F storage series, remained at that temperature until tested. Another series, designated as the constant 150° F storage series, was removed from the 70° F storage after the initial 24-hour period and stored at 150° F until tested. A third series, designated as combined storage series, after the initial 24 hours at 70° F, was placed in 150° F storage, then at the total elapsed time of 7, 28, and 90 days, the specimens were returned to the 70° F storage to be tested at the age of 1 year.

(c) TESTING OF SAMPLES

At the designated time of test the hardened specimen was freed from the glass of the vial and quickly ground in a mortar to such a fineness that no residue was left on the no. 30 sieve. The calorimeter charge was immediately weighed and its heat of solution determined. The latter was calculated as calories per gram of cement (or prehydrate) being tested.

2. STRENGTH TESTS

(a) DESCRIPTION OF TEST SPECIMENS

The compressive-strength specimens were made of prehydrated or untreated cements, Potomac River sand, and Potomac River gravel. The tests were made on 3- by 6-in. cylinders made from a 1:2:4 mix by volume, and a constant cement-water (C/W) ratio of 1.45. Gravel was taken in the proportions of 1 part of ¼ to ⅜ in. to 1¼ parts of ⅜ to ¾ in.

(b) MIXING AND STORAGE

Dry materials sufficient for 12 specimens were mixed thoroughly in a shallow pan, then the water was added and the mixing continued for 2½ minutes. All operations were performed in a constant-temperature room at 70±2° F. The specimens were fabricated in 3- by 6-in. tin-plated cylindrical cans. The cans were filled one-third full and the contents rodded with a bullet-pointed steel rod ½ in. in

diameter, and the same procedure was repeated for the two succeeding layers.

The molded specimens were cured at 70° F for 24 hours. At this age the cans were sealed with a bituminous material that was capable of withstanding a temperature of 170° F without flowing. Immediately after sealing, 12 specimens for each cement were stored at 70° F, and 21 specimens were stored at 150° F.

Three specimens from each storage were tested in compression at 7, 28, and 90 days, and 1 year. Also, 3 specimens from the 150° F storage were removed at 7, 28, and 90 days and placed in the 70° F storage; at a total age of 1 year they were tested in compression.

3. EXPANSION TESTS

Two types of expansion specimens were used in the study of linear changes of mortars stored in water and aqueous solutions of sodium sulfate.

(a) PLASTIC-MORTAR SPECIMENS—VARIABLE STORAGE

The first type of specimen was a bar 1 by 1 by 11 inches made from a 1:2.75 mix, by weight, of cement and pit-run Ottawa sand, using a C/W ratio of 1.88 by weight. The bars cast in molds contained glass plugs of 3/16 in. diameter by ½ in. long, placed in the center of each end, and protruding ⅛ in. beyond the end of the bar.

The bars, after 24 hours of curing in the molds at 70° F, were removed and placed in tap water at the same temperature. A set of 3 bars for each cement was cured in water for 7 days and then totally immersed in a 2-percent (anhydrous basis) aqueous solution of sodium sulfate. A second set of 3 bars was cured in water for 90 days and then immersed in a 10-percent solution of sodium sulfate. A third set of 3 bars was kept immersed in water for all ages of test.

Measurements of change of length were made with an Ames dial graduated to 0.0001 in. The dial was mounted rigidly in a steel frame. An invar-steel bar was used for the standard reference length. Measurements were made at 1, 2, 3, and 4 weeks, then every fourth week thereafter. The results are reported as percentage linear change based on the length of bar when put under test.

(b) VARIABLE MIXES—CONSTANT STORAGE

The second type of specimen, designed to be used in an accelerated test, was a bar 1 by 1 by 6 in., with two parallel faces indented with a triangular form [4] to increase the total area. Three mixes, 1:3, 1:4, and 1:5 parts of cement to parts of standard Ottawa sand, by weight, were used. The amount of mixing water was determined from the normal consistency according to Feret's relationship:

$$Y=\tfrac{3}{4}\frac{P}{n+1}+K,$$

where Y=percentage of water for mortar, P=percentage of water for normal consistency, n=parts of sand for 1 part of cement, and K=a constant (6.5 for standard Ottawa sand). The bars after molding were cured in a damp closet (100 percent humidity) at 70 ± 2° F for 24 hours, then removed from the molds, and cured in tap water at

[4] In casting the bars, there was placed in the center of the mold bottom a 3/16-in., 90° angle of brass equal to the length of the specimen. A similar angle was inserted likewise in the top of the filled mold, placed so that the ends of the angle legs were in the plane of the surface of the bar.

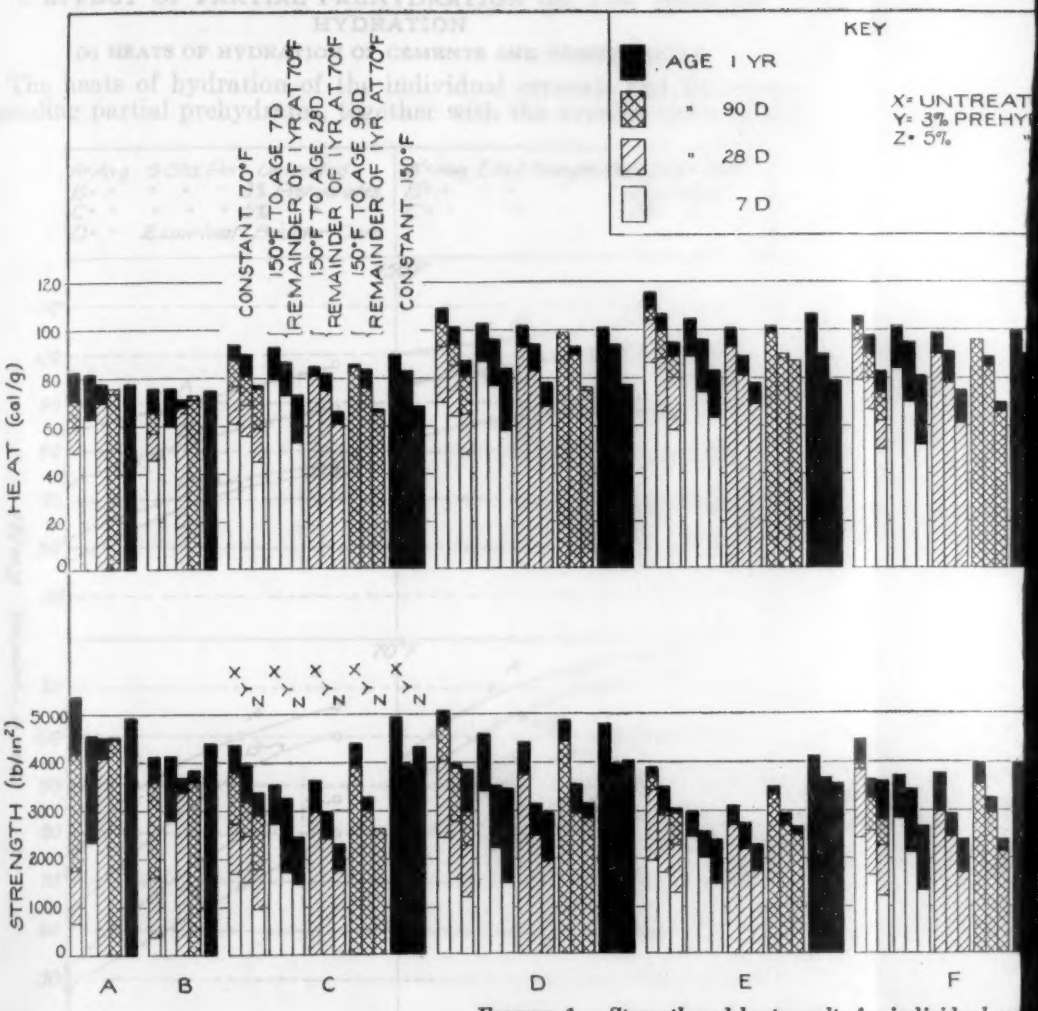
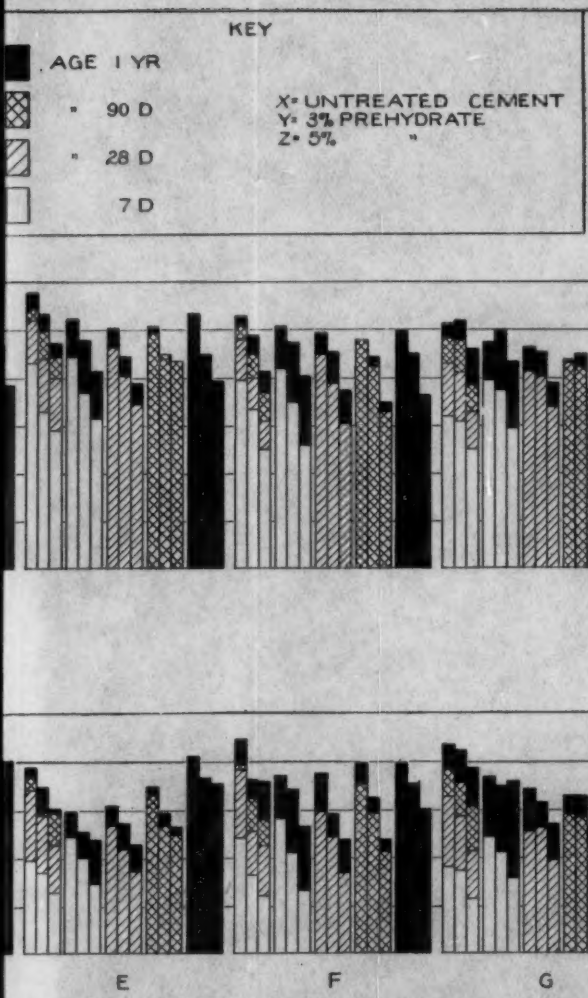


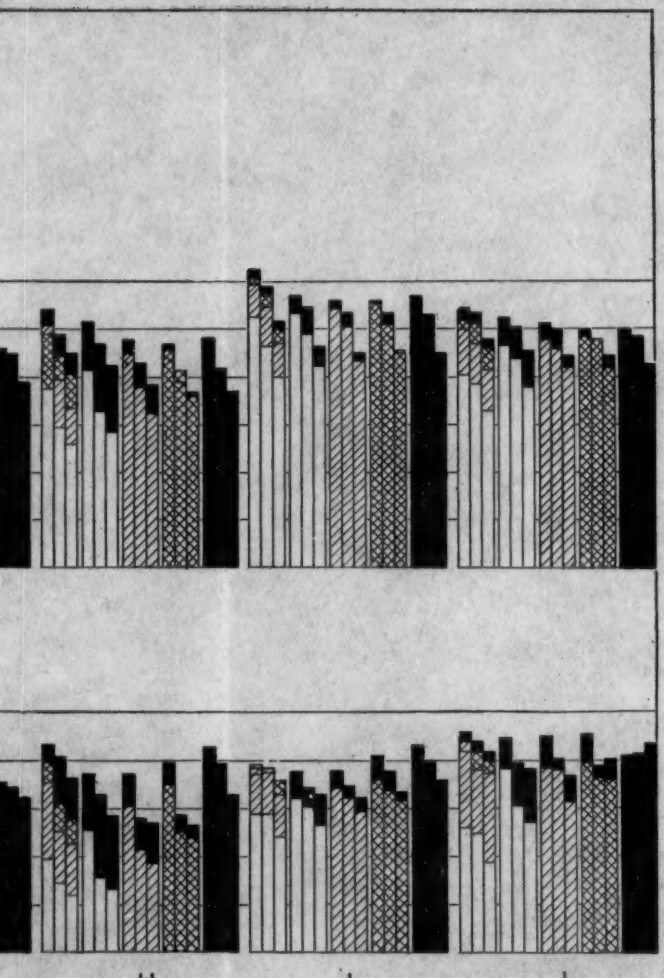
FIGURE 1.—*Strength and heat results for individual ce*

Complete legend given for cement C applies to all the cements.



rength and heat results for individual cements for different conditions

ven for cement C applies to all the cements.



...nditions of curing.

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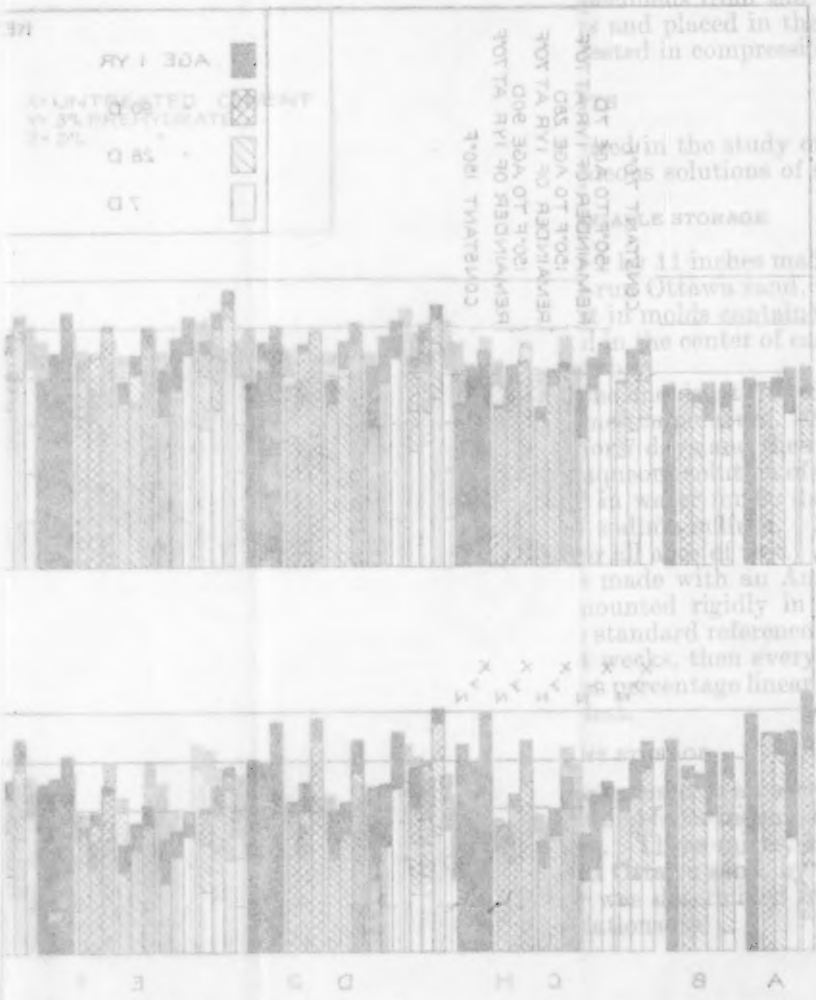

the same temperature for 48 hours. At this age (3 days) the bars were measured for length and placed in a 10-percent aqueous solution of sodium sulfate maintained at $70 \pm 2°$ F. Length changes were determined each week, and are expressed as percentage linear change based on the length of the bars at 3 days.

IV. HEAT OF HYDRATION RESULTS

1. EFFECT OF PARTIAL PREHYDRATION ON THE HEAT OF HYDRATION

(a) HEATS OF HYDRATION OF CEMENTS AND PREHYDRATES

The heats of hydration of the individual cements and the corresponding partial prehydrates, together with the average heats of the

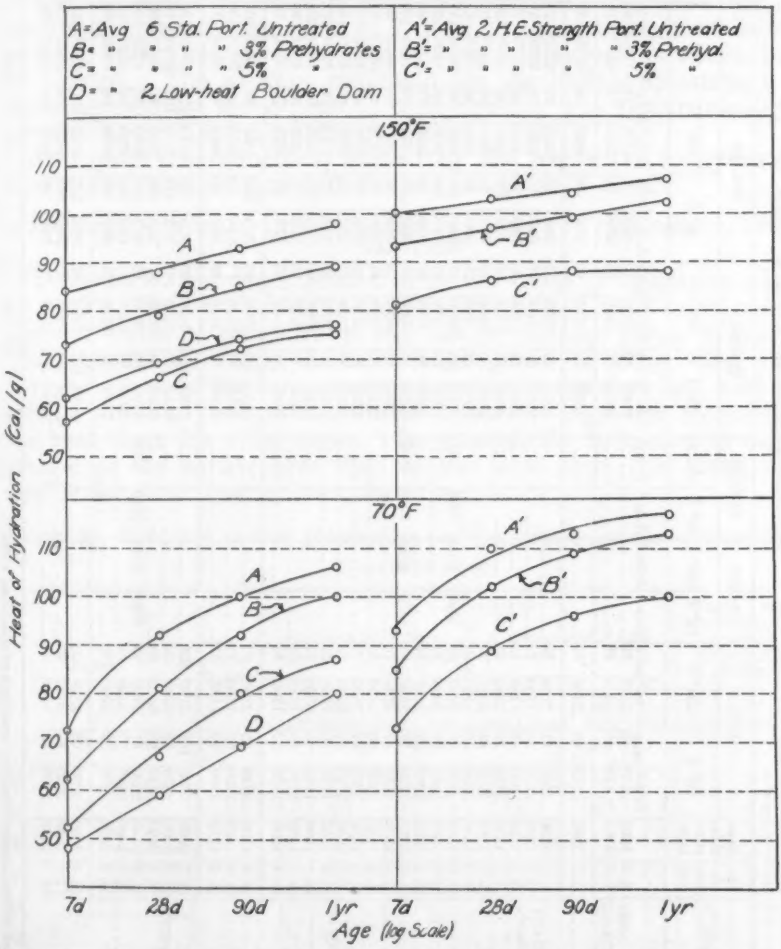

FIGURE 2.—*Average heats of hydration of untreated and prehydrated cements for 70 and 150° F curing.*

three types of cement, are given in table 2. Graphic representations of the individual heats of hydration are shown in figure 1, and the average heats of hydration of the three types are shown in figure 2.

TABLE 2.—*Strengths of 3- by 6-inch concrete cylinders, cured at different temperatures and ages, and heats of hydration of cements cured at corresponding temperatures and ages*

Cement	Type	Ignition loss	Specific surface	7 days				14 days		21 days		28 days				90 days				1 year				6 days at 150° F; 51 weeks at 70° F		27 days at 150° F; 48 weeks at 70° F		89 days at 150° F; 39 weeks at 70° F	
				70° F		150° F		70° F	150° F	70° F	150° F	70° F		150° F		70° F		150° F		70° F		150° F							
				lb/in.²	cal/g	lb/in.²	cal/g	lb/in.²	lb/in.²	lb/in.²	lb/in.²	lb/in.²	cal/g	lb/in.²	cal/g	lb/in.²	cal/g	lb/in.²	cal/g	lb/in.²	cal/g	lb/in.²	cal/g	lb/in.²	cal/g	lb/in.²	cal/g	lb/in.²	cal/g
A	Low heat	1.0	1890	660	49	2350	63					1760	60	4090	70	4180	71	4470	74	5360	83	4920	78	4540	82	4500	78	4530	76
B	do	1.3	1910	370	46	2800	60					1610	57	3380	68	3590	66	3600	73	4110	76	4390	75	4120	76	3670	71	3830	71
Avg A, B		1.2	1900	515	48	2570	62					1680	59	3730	69	3880	69	4030	74	4740	80	4660	77	4330	79	4090	75	4180	74
C	Standard portland.	.9	1680	1680	61	2730	80					2720	77	2970	81	3800	88	3910	85	4350	94	4940	90	3540	93	3630	85	4370	86
		2.9	1640	1510	56	1730	73					2470	69	2410	75	3190	81	3000	76	3950	90	3930	83	3250	87	2980	82	3270	84
		5.1	1630	950	45	1490	53					1790	59	1760	61	2900	76	2610	a 66	3370	77	4300	68	2440	73	2300	66	2610	67
D	do	1.1	1850	2410	70	3390	87					4000	93	3710	93	4760	103	4430	99	5060	109	4780	101	4570	103	4400	102	4870	98
		2.9	1880	1550	64	2200	77					2760	84	2480	83	3940	94	2930	90	3860	101	3940	94	3500	a 96	3110	94	3530	93
		5.2	1840	1190	48	1490	58					2260	65	1940	68	2980	81	2830	76	3830	87	4010	77	3440	84	2940	78	3120	74
E	do	1.0	1510	1950	86	2430	89	2560	2200	3050	2300	3410	104	2670	93	3680	109	3320	99	3870	116	4110	107	2960	105	3090	101	3470	102
		3.0	1580	1680	66	2000	74					2880	88	2170	81	2970	100	2670	88	3460	107	3660	90	2540	96	2710	89	2920	90
		5.3	1560	1260	58	1410	63					2250	80	1720	69	2930	89	2460	77	3020	95	3540	a 79	2380	83	2260	78	2650	77
F	do	1.5	1860	2400	79	2810	84	3050	2700	2910	2780	3820	96	2960	90	3950	102	3530	96	4470	106	3960	100	3710	102	3760	99	3980	96
		2.8	1850	1630	67	2100	70					2550	80	2430	78	3240	90	2930	85	3610	98	3510	90	3430	95	2900	91	3250	89
		5.3	1880	1200	50	1310	52					2250	62	1670	61	2800	74	2120	66	3600	83	3000	73	2650	81	2380	75	2380	70
G	do	1.8	1680	1800	64	2420	79					3260	86	2530	83	3820	97	2900	87	4360	103	3530	92	3680	95	3420	93	3270	88
		2.6	1680	1720	62	2100	75					2850	82	2620	81	3550	96	2820	85	4240	104	3410	90	3490	100	3150	91	3260	90
		5.1	1650	1130	50	1560	59					2120	66	1940	68	3060	77	2340	74	3870	92	3230	78	3580	87	2690	78	2600	75
H	do	1.1	1630	1930	75	2520	83					3520	98	3040	90	3950	102	3490	92	4320	108	4270	a 97	3700	103	3690	96	3940	94
		3.0	1590	1420	59	1520	66					2490	79	2110	76	3100	89	2510	83	4060	98	3940	84	3290	94	2780	86	2850	78
		5.4	1690	1170	52	1300	57					2240	67	1850	65	2770	81	2370	72	3610	90	3260	74	2830	85	2690	77	2620	74
Avg C to H		1.2	1700	2030	72	2720	84					3460	92	2980	88	3990	100	3600	93	4410	106	4270	98	3690	100	3670	96	3980	94
		2.9	1700	1590	62	1940	73					2660	81	2370	79	3330	92	2810	85	3860	100	3730	89	3250	94	2940	89	3180	88
		5.2	1710	1150	52	1430	57					2150	67	1810	66	2910	80	2460	72	3550	87	3560	75	2890	82	2540	75	2660	73
I	High-early	1.2	2500	2880	105	3190	107					3860	119	3420	109	3700	122	3610	111	3900	125	4300	114	3750	114	3780	112	4080	112
		3.0	2500	2870	93	3030	98					3840	109	3220	101	3750	115	3370	102	3770	118	3950	106	3430	109	3460	107	3760	107
		5.3	2420	2410	80	2640	85					3280	94	2920	87	3590	100	3150	91	3510	103	3570	90	3280	93	3220	90	3320	90
J	do	1.8	2540	2580	81	3830	93	3590	3760	3750	3760	4400	100	3840	96	4170	104	3950	97	4570	109	4070	100	4450	105	4480	102	4530	100
		2.8	2590	2480	77	3050	88					3800	94	3800	92	4150	103	3620	96	4370	107	4130	97	3940	101	4010	100	3880	98
		4.9	2590	1880	66	2700	76					3720	83	3120	84	4000	92	3600	84	4160	96	4320	85	3810	91	3670	89	4000	89
Avg I, J		1.5	2520	2730	93	3510	100					4130	110	3630	103	3940	113	3780	104	4240	117	4190	107	4100	110	4180	107	4310	106
		2.9	2550	2680	85	3040	93					3820	102	3510	97	3950	109	3500	99	4070	113	4040	102	3690	105	3740	104	3820	102
		5.1	2510	2150	73	2670	81					3500	89	3020	86	3800	96	3380	88	3840	100	3950	88	3550	92	3450	90	3660	90

a Extrapolated values necessitated by breakage of specimen vials.

These results show that increasing the amounts of prehydration caused successive reductions in the heats of hydration at all ages of both the standard portland and the high-early-strength cements. The 1-year value of the 3-percent prehydrate of cement G constituted a single exception to that behavior, but in forming that particular prehydrate, the loss on ignition (which already was 1.8 percent) was increased only 0.8 percent. The average reduction in the heat of hydration at 7 days of all the standard portland cements was, for the 3-percent prehydration, approximately 13 percent at both curing temperatures; the least individual reduction (other than cement G) was 8 percent. The average reduction of the 3-percent prehydrates of the high-early-strength cements was approximately two-thirds that of the same prehydrates of the standard portland cements.

The 5-percent prehydration of the standard portland cements caused an average reduction at 7 days of approximately 30 percent at both curing temperatures, the lowest individual reduction being 22 percent. The average reduction for the high-early-strength cements caused by the 5-percent prehydration was approximately 20 percent for both curing temperatures.

At 1 year the reductions caused by the respective prehydrations were approximately one-half the reductions at 7 days.

(b) REDUCTION IN HEAT OF HYDRATION PER PERCENT INCREASE IN LOSS ON IGNITION

The calories per gram reduction in the heats of hydration caused by each 1-percent increase in the loss on ignition were calculated for the two series of prehydrates and the results are given in table 3. These results show that the calories per gram reduction vary widely between cements for each percent increase in ignition loss, and that neither series of prehydrates uniformly affects a greater reduction of the heat than the other series. In general, the reduction in heat is greater at the earlier ages than at the later ages, this trend being similar for both curing temperatures.

TABLE 3.—*Reduction in heat of hydration for each percent increase of ignition loss*

[Calories per gram]

Cement	Increase in loss on ignition	Cured at 70° F for—				Cured at 150° F for—				Cured 1 year at combined storage; age when returned to 70° F storage—		
		7 days	28 days	90 days	1 year	7 days	28 days	90 days	1 year	7 days	28 days	90 days
	%											
C	2.0	2.5	4.0	3.5	2.0	3.5	3.0	4.5	3.5	3.0	1.5	1.0
	4.2	3.8	4.3	2.9	4.0	6.4	4.7	------	5.2	4.7	4.5	4.5
D	1.8	3.3	4.4	5.0	4.5	5.5	5.5	5.0	3.9	------	4.4	3.0
	4.1	5.4	6.8	5.4	5.4	7.0	6.1	5.6	5.9	4.6	5.9	5.9
E	2.0	10.0	8.0	4.5	4.5	7.5	6.0	4.5	8.5	4.5	6.0	6.0
	4.3	6.5	5.3	4.6	5.0	6.1	5.6	5.4	------	5.2	5.4	5.8
F	1.3	9.2	12.3	9.2	6.7	10.8	9.2	8.5	7.7	5.4	6.2	5.4
	3.8	7.6	8.9	7.4	6.0	8.4	7.7	7.9	7.2	5.5	6.3	6.9
G	.8	2.5	5.0	1.2	------	5.0	2.5	2.5	2.5	(a)	2.5	(a)
	3.3	4.2	6.0	6.0	3.3	6.0	4.5	3.9	4.2	2.4	4.4	3.9
H	1.9	8.4	10.0	6.8	5.3	8.9	7.4	4.8	------	4.8	5.3	8.4
	4.3	5.3	7.2	4.9	4.2	6.0	5.8	4.7	------	4.2	4.4	4.6
I	1.8	6.7	5.6	3.9	3.9	5.0	4.4	5.0	4.4	2.8	2.8	2.8
	4.1	6.1	6.1	5.4	5.4	5.4	5.4	4.9	5.9	5.2	5.4	5.4
J	1.0	4.0	6.0	1.0	2.0	5.0	4.0	1.0	3.0	4.0	2.0	4.0
	3.9	3.8	4.4	3.1	3.3	4.4	3.1	3.3	3.9	3.7	3.4	2.8
Avg	1.6	5.8	6.9	4.4	4.1	6.4	5.2	4.5	4.8	4.1	3.8	4.4
	4.0	5.4	6.1	5.0	4.6	6.2	5.3	5.1	5.4	4.4	5.0	5.0

[a] Gain.

A comparison of the values given in table 3 with the compound compositions of the cements fails to reveal any correlation between the reduction in heat and the amount of any one compound in the cements. Data on heats of solution also indicate that the reactions during steam treatment are not confined chiefly to one compound. Thus the reduction in heat of solution for each percent increase of loss on ignition by prehydration averaged 5.1 cal/g for the 3-percent series of prehydrates, and 4.4 cal/g for the 5-percent series. No individual value varied more than 0.9 cal from the average. Hence, the reaction was approximately the same for each cement, regardless of compound composition.

Davis and co-workers [4] from studies of aged commercial cements having high ignition losses suggest that for each percent ignition loss a correction of −6 cal/g be made in calculating the heat of hydration for the early ages and a correction of −3 cal/g be made for the 1-year value. The results of the present investigation, as presented in table 3, also indicate that a representative average value for 7 and 28 days is −6 cal/g, but for 1 year −4 cal/g is indicated. For individual cements, however, these values may need be reduced by 50 percent or increased by 100 percent.

(c) COMPARISON OF PREHYDRATED CEMENTS WITH BOULDER DAM CEMENTS

The 3-percent prehydrates of the standard portland and high-early-strength cements in all cases had considerably higher heats of hydration than the Boulder Dam cements. Of the 5-percent prehydrates of the standard portland cements, however, at the 70° F curing, three of the cements had 7-day heats of hydration comparable to the heats of the Boulder Dam cements. The average, however, of the standard portland cements cured at 70° F exceeded the average of the Boulder Dam cements. All the 5-percent prehydrates of the standard portland cements stored at 150° F had heats of hydration as low as or lower than the Boulder Dam cements cured at that temperature. The 5-percent prehydrates of the high-early-strength cements had, at both curing temperatures, higher heats than the Boulder Dam cements.

The upper limits for the heat of hydration, according to the specifications for Boulder Dam cements, were 65 and 75 cal/g at 7 and 28 days, respectively, the curing to be carried out at 100° F for these ages. If the curing is carried out at lower temperatures, as the 70° F of this investigation, it is generally assumed the heats would be somewhat lower and if conducted at higher temperatures, as the 150° F of this investigation, it is also frequently assumed they would be somewhat higher than if carried out at 70° F. The heats of hydration of the 5-percent prehydrates of the standard portland cements are well within the requirements of the Boulder Dam specification after either the 70 or 150° F curing. Later in the paper will be found discussions on the question of the effect of curing temperatures on the heat of hydration.

(d) CALCULATION OF THE HEATS OF HYDRATION

Methods of calculating heats of hydration from compound compositions and other data have been proposed by several investigators [3, 4, 13]. The compound compositions heretofore used have been those calculated according to the method of Bogue [11]. This

method assumes that the clinker is completely crystalline and that equilibrium is maintained between liquid and solid during cooling. Lea and Parker [8] have shown that the liquid present at the clinkering temperature does not maintain equilibrium with the preexisting solid on cooling and, therefore, propose corrections for the Bogue values. These proposed corrections of the calculated values are based on the assumption that (a) the liquid cools to a glass, or (b) the liquid crystallizes out independently at 1,400° C. The compound compositions of the cements used in this investigation were calculated by all three methods and are given in table 1.

All three sets of compound compositions were used in calculating the heats of hydration of the cements and prehydrates, using factors and corrections proposed by the Bureau of Reclamation [12]. These factors for the calories per gram of heat evolved for each percent of compound present in the cement are as follows:

Age, in days	C_3S	C_2S	C_3A	C_4AF
7	+1. 17	+0. 18	+2. 67	+0. 23
28	+1. 32	+. 43	+2. 54	+. 23
90	+1. 26	+. 63	+2. 43	+. 37

Corrections for loss on ignition and fineness were made as follows: for each percent ignition loss above 1 percent, 12 percent of the heat of hydration was subtracted, and for each 100 cm^2 of specific surface above 1,200 cm^2 the following amounts were added to the heats of hydration: at 7 days, 3 percent; at 28 days, 2.25 percent; and at 90 days, 1.50 percent. These calculated heats of hydration are listed in table 4, together with the observed heats of hydration for the same ages for both the 70 and 150° F curing.

TABLE 4.—*Comparison of calculated and observed heat of hydration values for 7, 28, and 90 days*

Cement	Loss on ignition	Specific surface	Age of test	Observed heat of hydration		Calculated heat of hydration based on compound composition calculated according to—		
				70° F storage	150° F storage	(a) Bogue method	(b) Liquid cools to glass	(c) Liquid crystallizes independently
	%	cm^2/g	*Days*	cal/g	cal/g	cal/g	cal/g	cal/g
A	1.0	1,890	7	49	63	72	50	Same as (a)
			28	60	70	89	68	
			90	71	74	96	76	
B	1.3	1,910	7	46	60	51	24	Same as (a)
			28	57	68	66	38	
			90	66	73	76	49	
C	0.9	1,680	7	61	80	86	61	Same as (a)
			28	77	81	98	73	
			90	88	85	96	73	
C	2.9	1,640	7	56	73	68	48	Same as (a)
			28	69	75	77	57	
			90	81	76	76	57	
C	5.1	1,630	7	45	53	48	34	Same as (a)
			28	59	61	54	40	
			90	76	----	51	39	

TABLE 4.—*Comparison of calculated and observed heat of hydration values for 7, 28 and 90 days*—Continued

Cement	Loss on ignition	Specific surface	Age of test	Observed heat of hydration		Calculated heat of hydration based on compound composition calculated according to—		
				70° F storage	150° F storage	(a) Bogue method	(b) Liquid cools to glass	(c) Liquid crystallizes independently
	%	cm²/g	*Days*	cal/g	cal/g	cal/g	cal/g	cal/g
D	1.1	1,850	7	70	87	99	69	97
			28	93	93	111	82	108
			90	103	99	107	79	106
D	2.9	1,880	7	64	77	82	57	80
			28	84	83	91	68	88
			90	94	90	87	64	86
D	5.2	1,840	7	48	58	58	40	57
			28	65	68	63	46	61
			90	81	76	59	43	58
E	1.0	1,510	7	86	89	117	74	107
			28	104	93	126	83	116
			90	109	99	122	81	112
E	3.0	1,580	7	66	74	93	59	86
			28	88	81	102	66	91
			90	100	88	101	63	87
E	5.3	1,560	7	58	63	63	40	58
			28	80	69	66	44	61
			90	89	77	62	41	56
F	1.5	1,860	7	79	84	109	74	104
			28	96	90	117	84	113
			90	102	96	113	80	107
F	2.8	1,850	7	67	70	92	64	88
			28	80	78	99	72	97
			90	90	85	99	68	91
F	5.3	1,880	7	50	52	65	44	62
			28	62	61	67	49	64
			90	74	66	63	45	60
G	1.8	1,680	7	64	79	100	67	97
			28	86	83	108	76	106
			90	97	87	106	73	103
G	2.6	1,680	7	62	75	90	60	83
			28	82	81	97	68	94
			90	96	85	95	66	94
G	5.1	1,650	7	50	59	61	41	59
			28	66	68	65	46	61
			90	77	74	63	44	61
H	1.1	1,630	7	75	83	106	77	101
			28	98	90	115	87	111
			90	102	92	114	84	108
H	3.0	1,590	7	59	66	83	61	79
			28	79	76	90	68	86
			90	89	83	89	65	84
H	5.4	1,690	7	52	57	59	43	56
			28	67	65	61	46	59
			90	81	72	60	44	57
I	1.2	2,500	7	105	107	144	100	137
			28	119	109	147	107	138
			90	122	111	136	92	125
I	3.0	2,500	7	93	98	122	84	115
			28	109	101	124	86	114
			90	115	102	111	75	102
I	5.3	2,420	7	80	85	90	62	85
			28	94	87	88	62	83
			90	100	91	78	53	72
J	1.8	2,540	7	81	93	99	68	
			28	100	96	106	77	Same as (a)
			90	104	97	102	74	
J	2.8	2,590	7	77	88	91	62	
			28	94	92	97	70	Same as (a)
			90	103	96	91	66	
J	4.9	2,590	7	66	76	72	49	
			28	83	84	74	54	Same as (a)
			90	92	84	68	50	

As can be seen from the tabulated results, the values calculated from the compound compositions according to Bogue, and the values calculated by assuming that the liquid crystallizes independently, are, in general, higher than the observed results, and the results calculated by assuming that the liquid cools to a glass are, in general, lower than the observed results. In no case, however, is there good agreement at all three ages between the calculated and observed values for either the 70 or 150° F storage.

Whether the lack of agreement is the fault of the factors, the corrections, or the calculated compound compositions, or a combination of all three, the investigation did not undertake to show. It might be noted, however, that in the present work the reduction in heat for each percent increase in the ignition loss of the cement was found, when expressed on a percentage basis, to be approximately 8 percent for 7 and 28 days and 5 percent at 90 days. Apparently the correction factor that was used (12 percent) is too high.

2. EFFECTS OF CURING TEMPERATURE ON HEATS OF HYDRATION

(a) CONTINUOUS STORAGE AT 70 AND 150° F

It is interesting to note that at 7 days the higher curing temperature produced higher heats of hydration for all the cements than the 70° F curing. At the age of 28 days, however, the high-early-strength and the standard portland cements both had lower heats of hydration at the 150° F curing temperature than at the 70° F. In general, these two types of cements, with increasing age, had increasingly greater heats of hydration at the lower curing temperature than at the higher temperature. The Boulder Dam cements, however, had greater heats of hydration at the higher curing temperature, not only at 7 days but also at 28 and 90 days. At 1 year the heat evolved at the lower curing temperature had exceeded that of the higher temperature, but by only a very small amount.

(b) COMBINED STORAGE

The results for heat of hydration obtained from the combined storage tests (i. e., the tests in which respective specimens were cured 24 hours at 70° F, then at 150° F for either 6, 27, or 89 days, then placed back at 70° F storage for test at the total age of 1 year) differ considerably from the results obtained from the continuous storage at 70° F. Of the specimens stored at 150° F for the 6-day period, before returning to the 70° F storage, the standard portland cements show an average decrease of 5.7 percent and the high-early-strength cements show an average decrease of 7.1 percent from the average value found for the continuous storage at 70° F for 1 year. The corresponding prehydrated specimens are affected approximately the same by this type of storage. The Boulder Dam cements show practically no decrease in heat in the combined-storage tests compared with the continuous-storage tests.

The cements cured at 150° F for 27 days, then at 70° F for the rest of the year, show somewhat greater decrease from the corresponding values obtained at the continuous storage at 70° F. The portland cements show an average decrease of 7.4 percent, the 3-percent prehydrates an average decrease of 11.0 percent and the 5-percent pre-

hydrate an average decrease of 13.7 percent. The high-early-strength cements had an average decrease of 8.5 percent from the value obtained at 70° F continuous storage; in this series the partial hydrates do not differ greatly from the original cements. In general, the values for heat of hydration obtained for the cements stored for 27 days at 150° F and then returned to 70° F for the remainder of the year, are very similar to the values obtained for a continuous storage at 150° F for the full year. The storage for 89 days at 150° F before returning to the 70° F storage caused even greater reduction in the heat of hydration for both the portland cements and the high-early-strength cements, as well as for their corresponding partial hydrates. Here, again, the prehydrates show somewhat greater reduction in heat than the corresponding untreated cements. In general, the cements that were cured at 150° F for 27 days or longer show as great, or greater, reduction in heat of hydration than if cured continuously at 150° F for the entire year.

Stenzel and Morris [10] found that a low-heat cement of the type used in Boulder Dam, cured continuously at 212° F, gave approximately the same heat of hydration at 14 days as that obtained in 6 months of standard curing. They suggest that "when it is desirable to know the ultimate heat developed by a cement, a curing temperature of 212° F would be advantageous in greatly accelerating the reaction." The results of this study likewise indicate that the 1-year heats of the Boulder Dam cements are but slightly affected by the curing temperature. The rest of the cements, however, show considerable difference in the amount of heat evolved at the two storage temperatures, in some cases the results being as much as 18 percent lower at the 150° storage than at the 70° F storage. These results indicate, therefore, that the 212° F curing would not give a true index of the ultimate heat of hydration of the portland or high-early-strength cements.

(c) STUDY OF DIFFERENCES IN HEAT EVOLUTION AT HIGH AND LOW CURING TEMPERATURES

Results given in table 5 and figure 3 show the effects on the heat of hydration at different ages caused by regrinding a cement to a high degree of fineness, and by curing cement specimens at 45° F as well as at 70 and 150° F. These results show that the heat evolved at the 45° F curing exceeded the heat evolved at the 150° F curing at an earlier age for the reground cement than for the original.

TABLE 5.—*Effect of 45, 70, and 150° F curing on heat of hydration*

Cement	Specific surface	Heat of hydration cal/g											
		Period of storage (days) at 45° F—				Period of storage (days) at 70° F—				Period of storage (days) at 150° F—			
		7	14	28	90	7	14	28	90	7	14	28	90
	cm²/g												
H	1670	56	70	79	95	73	87	95	103	82	86	87	91
H	2390	70	82	92	104	82	93	97	107	90	91	92	99
E	1510	59	74	87	100	95	------	104	109	80	------	93	99
F	1860	59	70	80	94	79	------	96	102	84	------	90	96
J	2540	71	78	101	102	81	------	100	104	93	------	96	97

Also, as can be seen from figure 2, the time required for the heat evolved at the 70° F curing to exceed the heat evolved at the 150° F curing was least for the high-early-strength cements, greater for the standard portland, and considerably greater for the Boulder Dam cements. Successive prehydrations also increased the age at which the heat evolved at 70° F exceeded that evolved at 150° F.

It is known [13] that the finer a cement is ground the greater is the early slope of the time-temperature curve, also as the curing temperature is raised the early slope of the time-temperature curve becomes greater [14]. Then, too, the time-temperature curve for high-early-strength cements has greater early slope than that of the standard portland cements, and prehydration decreases this slope [1]. These same factors increase the early slope of the time-temperature curve and also decrease the time required for the heat of hydration

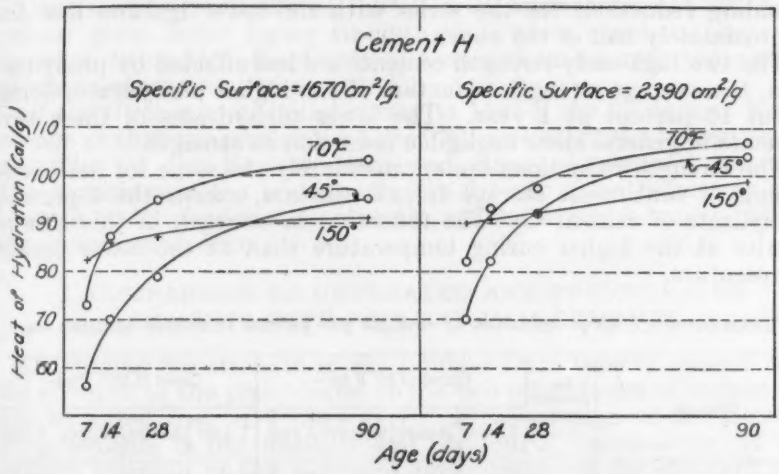

FIGURE 3.—*Heats of hydration at three different curing temperatures of cement* H *ground to two degrees of fineness.*

curve obtained at 70° F to cross the curve obtained at 150° F. It appears possible, therefore, that some relationship may exist between these two phenomena. Since an increased slope of the time-temperature curve indicates greater intensity of action during the initial hydration (setting), it is possible that when this activity is sufficiently great (caused by higher initial-storage temperature, grinding to greater fineness, or by using a quick-setting cement) the process of "setting" is speeded up. The hydrated material then precipitates so rapidly that unhydrated particles are coated with hydrated set material of such density that further hydration of the unhydrated particle is greatly inhibited. Hence, the lower evolution of heat at the higher curing temperatures for the later ages.

V. COMPRESSIVE-STRENGTH RESULTS

1. EFFECT OF PREHYDRATION ON THE COMPRESSIVE STRENGTH OF CONCRETE

The compressive strength results for concrete made of the cements as received, prehydrated to 3- and 5-percent ignition loss, and cured at 70° F, 150° F, and in combined storage are given in table 2 and figure 1.

Prehydration of these cements, in general, caused a reduction in strength, the higher prehydration resulting in the greater reduction. These reductions in strength are more pronounced, in terms of percentage, at the early ages, the average decrease of the six standard portland cements for the series with the higher ignition loss being about 40 percent at 7 days and about 20 percent at 1 year. Corresponding reductions for the series with the lower ignition loss are approximately half of the above.

The two high-early-strength cements are less affected by prehydration, the average strength reduction of the higher prehydrates being about 10 percent at 1 year. The lower prehydrates of these two cements in general show negligible reduction in strength.

The strength reductions are approximately the same for both conditions of continuous storage for all cements, except the 3-percent prehydrate of cement C. The reduction in strength in this case is greater at the higher curing temperature than at the lower curing temperature.

TABLE 6.—*Percentage reduction of strength per percent increased ignition loss*

Cement	Increased ignition loss	Cured at 70° F for—				Cured at 150° F for—			
		7 days	28 days	90 days	1 year	7 days	28 days	90 days	1 year
	%	%	%	%	%	%	%	%	%
C	2.0	5	5	8	5	18	9	12	10
	4.2	10	8	6	5	11	10	8	3
D	1.8	20	17	10	13	20	18	19	10
	4.1	12	11	9	6	14	12	9	4
E	1.9	7	8	10	6	9	10	11	6
	4.2	8	8	5	5	10	9	6	3
F	1.3	25	25	14	15	19	14	13	9
	3.8	13	11	8	5	14	12	11	6
G	.8	6	16	9	3	16	+4	4	4
	3.3	11	11	6	3	11	7	6	3
H	1.9	14	15	11	3	21	16	15	4
	4.3	9	8	7	4	11	9	7	6
Avg for C to H	1.6	13	14	10	7	17	10	12	7
	4.0	10	10	7	5	12	10	8	4
I	1.8	0	0	0	2	3	3	4	4
	4.1	4	4	1	2	4	4	3	4
J	1.0	4	14	0	4	20	1	8	+1
	3.1	9	5	1	3	10	6	3	+2
Avg for I, J	1.4	2	7	0	3	12	2	6	2
	3.6	7	5	1	3	7	5	3	1

The reductions in strength for both series of prehydrates were calculated to percentage reduction in strength per percent of increased ignition loss. The results are given in table 6. It is to be noted that in the calculation of these results small errors in strength for the 3-percent prehydrate cause large errors in the calculated values. Hence, in the 3-percent prehydrates, there are a number of erratic

values at different ages. The general trends for individual cements are more uniform for the 5-percent prehydrates.

The percentage reductions are in general greatest at 7 days and decrease with age for both conditions of curing.

With the exception of the two high-early-strength cements and several of the values in cements C and E, the 3-percent prehydrates show greater strength reductions per percent increase in ignition loss than the 5-percent prehydrates.

It is possible that the greater percentage reduction shown by the 3-percent prehydrates is due to a greater percentage of combined water per percent of ignition loss. From Meyers' [2] results on one cement it is observed that the percentage of combined water (per percent of ignition loss) increases with decreasing ignition losses.

2. EFFECT OF COMBINED STORAGE ON STRENGTH

Concrete cured initially at 150° F, with later storage at 70° F, in general gives lower 1-year strength than when cured continuously at either 70 or 150° F. Davis and co-workers [4] reported similar effects on concrete cured at 110° F.

Of the three ages of initial curing at 150° F the 27 days of initial storage at that temperature, resulted, in general, in the lowest 1-year strengths for the Boulder Dam and standard portland cements. The variations in the 1-year strengths for any given cement or prehydrate under combined storage are, on the whole, however, within the experimental error.

3. COMPARISON OF UNTREATED AND PREHYDRATED CEMENTS WITH BOULDER DAM CEMENTS

Comparing the strength of the Boulder Dam type of cement with the strength of the prehydrates of the two other types of cements, it will be noted that at 7 days at 70° F the average of the Boulder Dam cements is but one-half and one-fourth, respectively, of the average strength of the 5-percent prehydrates of the standard and high-early-strength cements; at 28 days the Boulder Dam cements are still lower, but by 90 days they have exceeded the strength of the other cements. Compared with the 3-percent prehydrates the Boulder Dam cement strengths are relatively lower than when compared with the strengths of the 5-percent prehydrates. Although the strengths of the Boulder Dam cements when cured at 1 year at 70° F are considerably better than the strengths of either of the prehydrates of the other types of cement, it should be noted that the strength of one Boulder Dam cement is of the same order as the untreated cements and the other Boulder Dam cement is distinctly better. It is hence evident that such high-silica cements as those of the Boulder Dam type show most excellent strength increases with age, the average increase at 1 year being about 8 times the 7-day strength. But with the standard type of cement the year strength averages about 3 times the 7-day strength, while with the high-early cements it averages somewhat less than twice the 7-day strength.

This relation for the three types of cement is somewhat different for the 150° F curing. The Boulder Dam type of cement develops much more strength at early ages at higher temperature than do the two other types. But this rate is not maintained at the late ages. The

increase between the 7-day and 1-year strength of the Boulder Dam cements is but 0.85 that of the 7-day strength, while for the standard cements it is 1.5, and for the high-early-strength cements it is 0.5.

In resumé, from the strength viewpoint, the prehydrated cements of either the standard or high-early-strength type are distinctly better at 7 days, if cured at 70° F than the Boulder Dam type; cured at 150° F the strengths of the latter are slightly above those of the prehydrated standard cements and slightly below those of the prehydrated high-early-strength type. This relation changes somewhat with age, and while all types at the age of a year show good strength gains at both temperatures, the high-silica Boulder Dam cements have gained strength at such a greater rate that they are distinctly stronger than the others.

VI. COMPARISON OF HEAT AND STRENGTH RESULTS

1. CONTINUOUS STORAGE AT 70 AND 150° F

Although, as shown in figure 1, the heats of hydration and the strengths both increase with age, no mathematical relationship exists between the heat and strength data for these cements. This is to be expected because the compounds in the cement do not contribute to heat and strength in the same relative proportions.

The rate at which the compressive strength develops varies markedly from the rate at which the heat of hydration develops at different ages. In table 7 the average percentages of the 1-year strength and 1-year heat that was developed during the first 7 days and also between 90 days and 1 year are given for the standard portland cements.

TABLE 7.—*Comparison of the average heats of hydration and compressive strengths of the standard portland cements developed at various ages*

Property measured		Percentage of 1-year value developed during first 7 days			Percentage of 1-year value developed after 90 days		
		As received	3% prehydrate	5% prehydrate	As received	3% prehydrate	5% prehydrate
Heats of hydration	70° F	70	62	60	6	8	7
	150° F	86	82	73	4	4	5
Compressive strengths	70° F	46	42	32	9	15	19
	150° F	62	53	41	15	24	32

As can be seen from table 7, the heat developed during the first 7 days is proportionately much greater than the strength, but between 90 days and 1 year the heat developed is comparatively small, whereas the strength, particularly of the prehydrated cements, shows considerable gain.

The successive prehydrations of the high-early-strength cements caused successive reductions in the heat evolved at all ages, but in the case of the strengths there were some exceptions to this order.

The two Boulder Dam cements cured at 70° F developed, at the age of 7 days, low strengths but the heats developed were proportionately high. At later ages the strengths developed were accompanied by a relatively low evolution of heat. Cured at 150° F these cements

attain strengths comparable to the standard portland cements cured at the same temperature, but evolve less heat.

2. HEATS AND STRENGTHS FOR COMBINED STORAGE

All cements and corresponding hydrates, after an initial 6 days' curing at 150° F, show a substantial gain in both the heats and the strengths. The 1-year results for heats are intermediate between the 1-year results for continuous 70 and 150° F curing, whereas the strengths in general are lower than those obtained from a continuous curing at either temperature. Results obtained from an initial 27 days of curing at 150° F show a decrease in the 1-year heats, and, in general, a decrease in the strengths, compared with the 1-year results for an initial 6 days at 150° F. The 89-day initial curing at 150° F results in lower 1-year heats of hydration, but the strengths remain the same or slightly higher than for the other two combinations of storage.

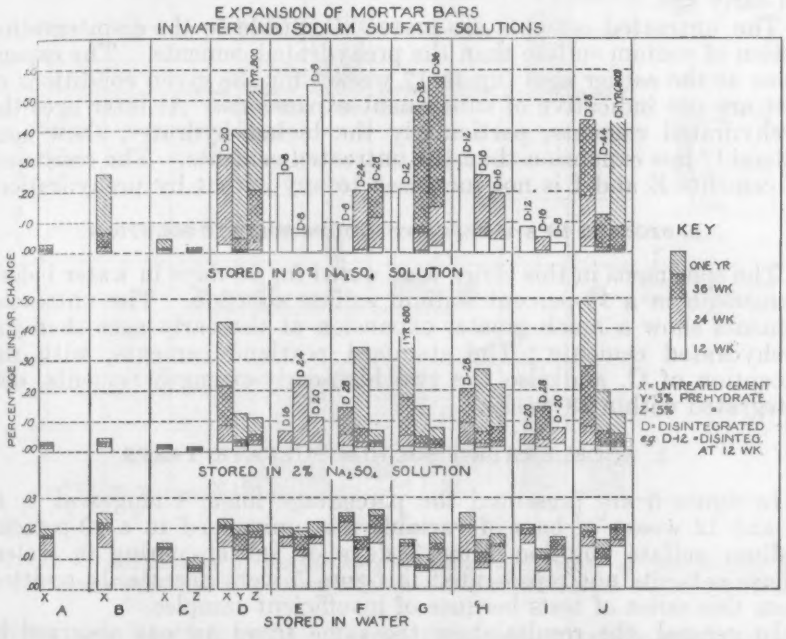

FIGURE 4.—*Expansion of mortar bars, made of prehydrated and untreated cements, during immersion in water and sodium sulfate solutions of different concentrations*

VII. EXPANSION RESULTS

1. CONSTANT MIX, VARIABLE STORAGE

The expansion results for the 1:2.75 mortar bars are presented graphically in figure 4. As explained by the key, the respective series of columns represent the linear change of bars in water storage, in 2-percent and in 10-percent solutions of sodium sulfate.

(a) EXPANSION IN WATER STORAGE

The percentage of linear change of any one of the cements does not show a marked deviation from the average linear change. In general, the cements prehydrated to 3-percent ignition loss show a slightly lower expansion than the untreated cements or the cements of 5-percent ignition loss, the difference being approximately 0.005 percent. A change of this magnitude may be due to a number of factors other than a change of the property of the cement. The 5-percent prehydrates show approximately the same linear change as the untreated cements.

(b) STORAGE IN A 2-PERCENT SODIUM SULFATE SOLUTION

Cements stored in a 2-percent sodium sulfate solution after the initial 7 days' storage in water show marked differences in expansion. Cements A, B, and C are highly resistant to the aggressive action of sodium sulfate, whereas cements E and I disintegrate at an early age.

The untreated cements are more susceptible to the disintegrating action of sodium sulfate than the prehydrated cements. The expansions at the earlier ages (up to 12 weeks) for the given conditions of test are not indicative of subsequent expansions. At later ages the prehydrated cements, particularly the higher hydrates, show considerably less expansion than the untreated cements. The resistance of cements E and I is not increased to any extent by prehydration.

(c) STORAGE IN A 10-PERCENT SODIUM SULFATE SOLUTION

The specimens in this series were cured for 90 days in water before immersion in a 10-percent sodium sulfate solution. The untreated cements show a much greater expansion at the early ages than the prehydrated cements. The standard portland cements, with the exception of C, and also the two high-early-strength cements, disintegrated within 28 weeks.

2. ACCELERATED SODIUM SULFATE TESTS

In figure 5 are presented the percentage linear changes at 1, 4, 8, and 12 weeks of bars of variable mix, immersed in a 10-percent sodium sulfate solution after 3 days of initial curing in water. Those cements not represented in figure 5 were necessarily omitted from this series of tests because of insufficient samples.

In general, the results show the same trend as was observed in the preceding test, namely, a greater resistance to sodium sulfate by the prehydrated cements.

The untreated cements all show the same variation in expansion with a change in mix; that is, the leaner the mix the greater the expansion. This is apparent at all ages of test. The 5-percent prehydrates do not follow such a trend, cements D, G, and H showing greater expansions with increasing richness of mix.

3. SULFATE RESISTANCE ACCORDING TO THE MERRIMAN TEST METHOD

Pats of neat pastes of the untreated and of the prehydrated cements were tested according to the Merriman method [15]. The best deportment was shown by cement A. This cement showed no effect

until 1½ years, then a slight expansion and cracking of the edges was noted. Cements B and C showed no effects until about 1 year, when slight expansion was noted on the edges. Cement E was the only one to fail before 4 weeks. This same cement when 3-percent prehydrated showed no effects until at the age of 23 weeks; when 5-percent prehydrated, disintegration started at 43 weeks. Cement I failed in 8 weeks. Prehydration of this cement affected its resistance only slightly. Cement F failed in 13 weeks, while both degrees of prehydration extended the failing age to about 40 weeks. Cement H failed in 15 weeks; 3-percent prehydration extended its life to 67 weeks, and at 75 weeks there is no material effect on the 5-percent prehydrated samples. Of the three other cements, two failed at 40 weeks and the other at 55 weeks. Prehydration to the extent of 3 percent extended the time of failing

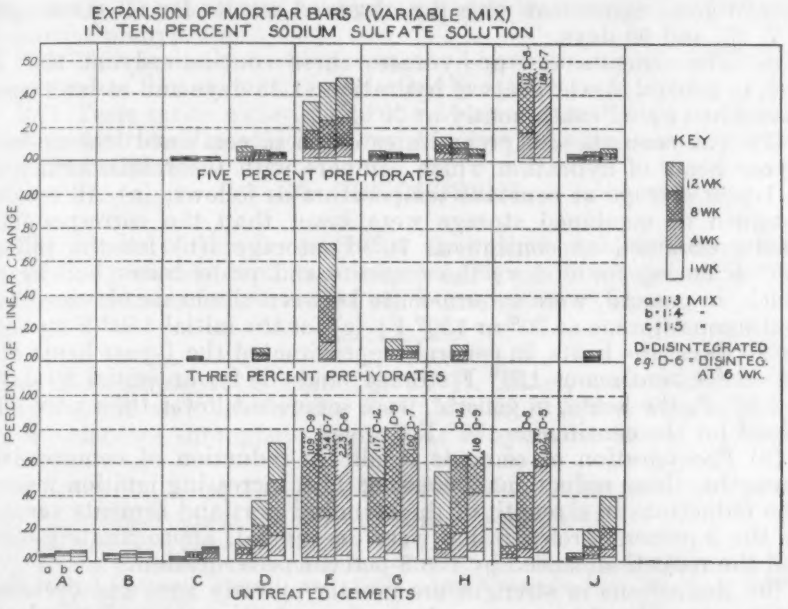

FIGURE 5.—*Expansion of mortar bars (varying mix), made of prehydrated and untreated cements, during immersion in a 10-percent sodium sulfate solution.*

from about 2 to 4 months. Five-percent prehydration extended the failing age another 2 to 4 months.

VIII. SUMMARY

(1) An increase in the loss on ignition of cement as a result of steam prehydration is accompanied by a decrease in the heat of hydration. For the standard portland cements this decrease at 7 days averaged approximately 13 and 30 percent, respectively, for the 3- and 5-percent prehydrates. At 1 year the average percentage decrease was approximately one-half that of the 7-day decrease. For the high-early-strength cements the 3- and 5-percent prehydration caused an average reduction of 8 and 20 percent, respectively, at 7 days, and 3 and 11 percent, respectively, at 1 year.

(2) The percentage reduction in heat of hydration caused by the prehydration of the cements was approximately the same for the 150° F curing as for the 70° F curing.

(3) The calories per gram reduction in heat of hydration for each percent increase in loss on ignition varied widely between individual cements; the average reduction for all the cements at the ages of 7 and 28 days being approximately 6 calories, and the average reduction at 1 year being approximately 4 calories.

(4) The standard portland cements, prehydrated to have a loss on ignition of approximately 5 percent, had heats of hydration at both curing temperatures for the ages of 7 and 28 days that were well within the upper limits named in the specification for the low-heat Boulder Dam cements.

(5) Heats of hydration, calculated from empirical factors, together with corrections for loss on ignition and specific surface, are in no case in good agreement with the observed results for all three ages of 7, 28, and 90 days.

(6) The cements and prehydrates cured continuously at 150° F had, in general, lower heats of hydration at 28 days and at later ages than when cured continuously at 70° F.

(7) The cements and prehydrates cured in combined storage had 1-year heats of hydration which compare with the results obtained at 1-year storage at constant temperature as follows: (a) All results obtained at combined storage were lower than the corresponding results obtained at continuous 70° F storage; (b) for the initial 150° F curing for 6 days the cements and prehydrates had heats which, in general, were intermediate between the heats obtained for continuous storage at 70° or 150° F; (c) for the initial 150° F storage for 27 days, the heats, in general, approximated the 1-year heats obtained for continuous 150° F storage; and (d) for an initial 89 days at 150° F, the heats, in general, were somewhat lower than were obtained for the continuous 150° F storage.

(8) Prehydration of cements results in reduction of compressive strengths, these reductions increasing with increasing ignition losses. The reductions in strength of the standard portland cements caused by the 3-percent prehydration were, in general, approximately one-half the reduction caused by the 5-percent prehydration.

(9) Reductions in strength are greater at early ages and decrease with age. The 5-percent prehydration of the standard portland cements caused approximately 40-percent reduction at 7 days and approximately 20 percent at 1 year. The high-early-strength cements, although less affected by prehydration, follow the same trend.

(10) For continuous storage, the reductions in strength caused by prehydration are, in general, approximately the same for both storage-temperatures, 70° and 150° F.

(11) The percentage reductions in compressive strengths per percent increase in ignition losses are, in general, greater at 7 days and then decrease with age. The 3-percent prehydrates of the standard portland cement had, in general, greater proportional reductions in strength than the 5-percent prehydrates.

(12) An initial curing at high temperature (combined storage) results in lower compressive strengths at 1 year than obtained at continuous curing at either 70° or 150° F.

(13) A comparison of the compressive strengths of the Boulder Dam cements with the compressive strengths of the 5-percent prehydrates of the standard portland cement—the group that had heats of hydration that would pass specifications for low heat Boulder Dam cements—shows that for 70° F curing the prehydrate strengths averaged 51 and 22 percent greater for 7 and 28 days, and 25 percent less for 90 days and also at 1 year than the Boulder Dam cements. For 150° F curing the prehydrate strengths averaged 44, 51, 39, and 24 percent less, respectively, for the ages of 7, 28, 90 days, and 1 year than the Boulder Dam cements.

(14) Mortars of prehydrated and untreated cements show approximately the same expansion in water storage.

(15) Prehydration increased the resistance of all the portland cements, with the exception of the two cements with highest tricalcium aluminate content, to the disintegrating action of sodium sulfate. In general, the 5-percent prehydrates were more resistant than the 3-percent prehydrates.

(16) Mortars of untreated cements show greater expansion for leaner mixes, but no trend is indicated for prehydrated cements.

(17) Tests made according to the Merriman method also showed that prehydration increases the resistance of the cement to the action of sodium sulfate.

IX. CONCLUSION

The results of this investigation show that prehydration can be successfully used to produce a low-heat, high sulfate-resistant cement without seriously impairing its other properties.

Acknowledgement is made to P. H. Bates, who planned this investigation and directed the work; also to J. Arthur Swenson, who gave assistance throughout in the heat of hydration tests.

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A STUDY OF THE WEATHERING QUALITY OF ROOFING FELTS MADE FROM VARIOUS FIBERS

By O. G. Strieter [1]

ABSTRACT

An investigation to determine the relative effect of different fibers on the life and serviceability of asphalt-saturated and coated felts has been in progress at the National Bureau of Standards since 1926. Experimental felts composed of varying proportions of the usual felt-making fibrous materials and some with a high content of substitutes not employed commercially in roofing felts, were made for the investigation.

The papermaking materials employed were no. 2 roofing rags, old jute and manila bagging, old newspapers, sulphite pulp, and finely ground wood sawdust. Some of the felts were made on a commercial cylinder felt-making machine, while others were made on a small fourdrinier paper machine, but all the felts were saturated and coated in commercial roofing mills, and thus converted into roofing material.

Measurements were made on the dry or unsaturated felts, on the saturated felts, and on the finished roofing. On the last two products the measurements were made before and after exposure outdoors. These measurements show that there was no significant difference in the resistance to weathering of asphalt roofing which may be attributed to the kind of fiber or combination of fibers employed.

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I. INTRODUCTION

The paper felts used as the base of asphalt roofing materials are made of rags, with or without the addition of substitutes. Owing to the increased cost of rags in recent years, more extensive use has been made of substitute materials in admixture with the rag stock. In this paper are reported the results of an investigation to determine the effect of different fibers on the life and serviceability of roofing materials.

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Paper felts composed of varying mixtures of the usual felt-making fibrous materials, and with a high content of substitutes, were made for this investigation. The papers produced were subsequently converted into asphaltic roofing materials. In order to determine the effect of weathering upon the various fibers, the tensile and tearing strengths and other physical properties of these roofing materials were determined before and after exposure outdoors.

The production of these roofing materials was described in a previously published paper. [2] The present paper is concerned with the behavior of these materials toward weathering. For the sake of completeness some of the information and data in the previous paper are repeated in the present paper, but the commercial felts (F series) have been renumbered.

II. DESCRIPTION OF MATERIALS

For this investigation, unsaturated felts, saturated felts, and smooth-surfaced roofings were prepared. Dry or unsaturated felt is made by pulping fibrous material and converting the prepared pulp into a dry, continuous sheet on a paper machine. For preparing saturated felt, the felt is impregnated with asphalt by running the sheet through a tank containing hot asphalt. In the industry this latter operation is called saturation, the asphalt employed is termed the saturant, and the impregnated felt is known as saturated felt. The smooth-surfaced roofing is prepared by coating both sides of the saturated sheet with asphalt (coating asphalt), and then sifting talc, sand, or other granular material on the surface. The details of the manufacturing process of felts and of the saturated and coated materials were described in the paper cited above and so need not be given here.

The various stocks that were used in the production of the felts were agreed upon by a committee of the Dry Felt Manufacturers Association in cooperation with the Asphalt Shingle and Roofing Institute. Felts for roofing materials are usually made from cotton rags of varying quality. For the present investigation it was the intention to combine no. 2 roofing rags with large amounts of substitutes, and, in order to make the roofings comparable, the felts were to be impregnated (saturated) with asphalt to 140 percent by weight. This degree of saturation was formerly standard practice, although at the present time the requirements are much higher.

The manufacture of the felts was undertaken on a commercial-size cylinder machine, of Arrowhead Mills, Inc., Fulton, N. Y. Thirteen different felts were manufactured there and are identified in the accompanying tabulations as F1 to F13, inclusive. These felts were saturated and coated with asphalt at the plant of McHenry-Millhouse Co., Fulton, N. Y.

Owing to the inability to produce felts containing as much "substitute material" as was desired on the available machine at Arrowhead Mills, arrangements were made with the National Bureau of Standards to prepare other felts on the semicommercial 29-inch fourdrinier machine in the paper laboratory of the Bureau in Washington, D. C. These additional felts are identified in the accompanying tabulations as B1 to B6, inclusive. They were saturated and coated with asphalt at the plant of the Ruberoid Co., Joliet, Ill.

[2] BS J. Research 2, 1001 (1929) RP67.

The asphalt saturants and coatings used at the two plants were from different sources. However, all the felts of each series were saturated and coated with the same materials. The characteristics of the saturant and coating asphalts employed in each series of felts are shown in tables 2 and 4.

III. OUTDOOR EXPOSURES

For purposes of test, specimens of the saturated felts of both series, together with their corresponding coated products (smooth-surfaced roofing), were exposed outdoors at an angle of 45 degrees, facing south, on specially constructed racks provided by the Asphalt Shingle and Roofing Institute, and located on the roof of the Industrial Building, National Bureau of Standards, Washington, D. C. (fig. 1).

The faces of the racks were 36 inches high and were so constructed that the boards formed a continuous surface; hence the back sides of the specimens of roofing materials were not exposed to the weather. To prevent adhesion of the back sides of the specimens, the racks were first coated with a suspension of talc in water. The specimens of roofing materials (36 inches in length), with an overlap of one inch between adjacent pieces, were fastened to the racks with roofing cleats. There were 19 varieties of saturated felts and 19 varieties of smooth-surfaced roofing exposed in this manner. A sufficient number of specimens of each of these varieties were placed on the racks so they could be removed and tested at certain intervals of time. In all, enough samples were placed on the racks so that seven complete series of tests could be made.

The relative behavior of the materials toward weathering was determined from changes in weight, tensile strength, and other measurable properties, brought about by exposure. The results of these measurements were supplemented by opinions based on visual examination.

IV. MEASUREMENTS ON MATERIALS BEFORE EXPOSURE

The physical properties[3] of the dry or unsaturated felts, the saturated felts, and the smooth-surfaced roofings before exposure are discussed under the following headings:

1. DRY OR UNSATURATED FELTS

Table 1 shows the fiber composition, the weights, thicknesses, saturability tests, the tensile and tearing strengths, and the ash content of the different felts.

[3] The methods of test were described in the previously published paper, BS J. Research 2, 1001 (1929) RP67. See also Herbert Abraham, Asphalt and Allied Substances, 3d ed. (D. Van Nostrand Co.). Also Standard Methods of Tests of the Technical Association of the Pulp and Paper Industry, 122 E. 42d St., New York, N. Y.

TABLE 1.—*Test data on the dry felts*

a	b		c	d	e	f	g	h	i	j	k
Sample	Composition		Wt 108 sq ft	Thickness	Kerosene test	Xylol test	Tensile Strength of strips 1 in. wide [1]		Tearing test [1]		Ash
	Amt. by wt	Material					Machine direction	Across machine direction	Machine direction	Across machine direction	
	%		lb	in.	%	sec	lb	lb	g	g	%
F1	100	Rag	11.0	0.053	203	25	37	19	38	26	6.8
F2	60	Rag	11.2	.053	189	25	45	21	48	34	5.3
	40	Sulphite									
F3	80	Rag	12.3	.062	200	21	40	21	54	34	5.3
	20	Sulphite									
F4	90	Rag	12.6	.067	220	19	40	20	56	35	5.8
	10	Ground wood									
F5	80	Rag	12.1	.068	240	16	35	19	47	32	6.0
	20	Newspaper									
F6	90	Rag	11.4	.063	219	17	37	18	48	30	5.4
	10	Newspaper									
F7	80	Rag	11.4	.059	210	18	38	18	44	31	6.5
	20	Mixed papers									
F8	90	Rag	10.3	.054	212	22	37	18	42	26	6.3
	10	Mixed papers									
F9	60	Rag	11.4	.058	217	28	34	17	43	26	6.4
	40	Burlap									
F10	80	Rag	10.8	.057	221	28	33	17	44	22	6.2
	20	Burlap									
F11	70	Rag	11.0	.060	231	17	33	16	45	28	6.6
	30	Carpet									
F12	85	Rag	10.8	.058	238	16	31	15	41	22	7.1
	15	Carpet									
F13	80	Rag	10.5	.059	231	16	35	18	42	29	6.0
	20	Ground wood									
B1	100	Rag	9.8	.042	162	69	34	25	31	24	7.1
B2	60	Rag	10.0	.050	187	61	29	18	29	20	5.6
	30	Newspaper									
	10	Sawdust									
B3	10	Rag	9.9	.054	191	55	37	27	24	16	2.1
	60	Newspaper									
	30	Sawdust									
B4	60	Rag	9.0	.041	161	66	38	27	32	25	5.8
	20	Bagging									
	20	Newspaper									
B5	67	Bagging	9.1	.045	187	37	40	31	32	23	5.6
	33	Newspaper									
B6	100	Bagging	9.3	.049	217	17	33	27	32	24	6.0

[1] These results are the average of 10 determinations.

The fiber composition of the felts given in the table is the "mill furnish", i. e., the percentages by weight of the raw materials furnished to the beater in the manufacture of the felts. The microscopic analysis of the fiber composition of these felts has been described elsewhere.[4]

Felt weights are given on the basis of 108 square feet. The felts are customarily spoken of as "light", "medium", or "heavy", depending on the weight. Those given in the table are considered medium. The strength tests—tensile and tearing—and the thickness measurements were made under the standard atmospheric conditions for paper testing, 65-percent relative humidity and 70° F. The tensile-strength measurements were made on a Scott tensile

[4] R. E. Lofton, *Determination of the fiber composition of roofing felts*, Paper Trade J. 84, no. 14, p 57-58 (Apr. 7, 1927).

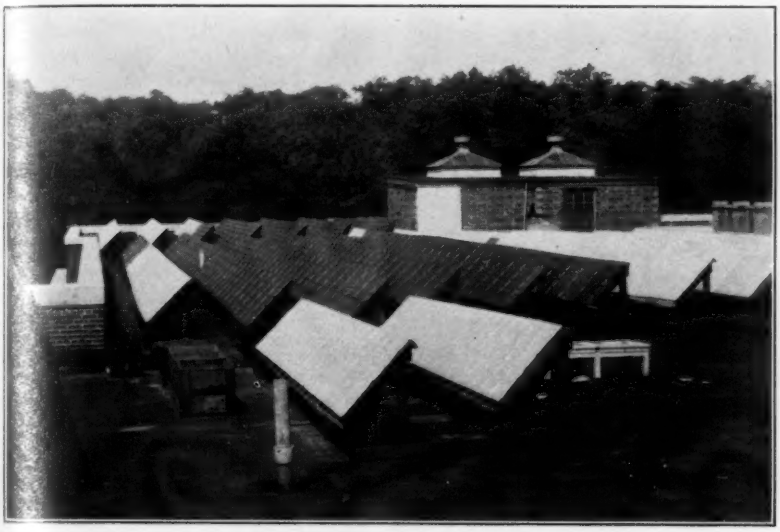

FIGURE 1.—*Exposure racks*

The dark samples are the saturated felts, the light ones are the smooth-surfaced roofing samples.

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tester. The tearing tests were made with the Elmendorf tearing tester, but the standard design of this instrument is not adapted to heavy material, such as roofings and saturated felts, so a modification had to be made before these materials could be tested.[5] The modification consisted in doubling the weight of the swinging sector by the addition of a brass plate and multiplying the scale readings by 2.

The kerosene and xylol tests are absorption tests and were made to determine the saturating quality of the felts. The object of the kerosene test is to obtain the maximum saturating capacity of the felts. A sample of the dry felt is saturated with a measured volume of kerosene in order to determine the amount of voids. From the results obtained the so-called theoretical maximum percentages of asphalt saturation of the sheet are computed. The computation involves the weight of the sample, the volume of kerosene the sample absorbs, and the specific gravity of asphalt, which is assumed to be 1.03.[6]

The xylol test supplements the kerosene test and is used to determine the relative speed at which saturation will take place. The test consists in immersing in xylol a strip of the felt 15 cm wide to a marked depth of 1 cm, and measuring the time required for the xylol to rise to another mark 3 cm higher.

Pliability tests were made on the felts but are not recorded in the table. The tests, however, showed that the felts of the B series were somewhat less pliable than those of the F series, with the exception of B1, an all-rag felt. Felt B3 was particularly lacking in pliability and so was considered not adaptable to commercial use, but this lack of pliability had no deleterious effect upon the resistance of the saturated and coated products to weathering.

The main difference between the two series of felts, aside from fiber composition, was that the felts of the B series were more compact and paper-like than the felts of the F series. This compactness was due to fiber composition and to a slightly prolonged beater operation which brushed-out the fibers and caused them to become shorter and slightly gelatinized on the surface. Such fibers make a well-felted, smooth-surfaced sheet. The felts of the B series were about 16 inches in width, those of the F series were 32 inches in width.

No difficulty in the saturating and coating operations was observed with any of the felts of either series.

2. SATURATED FELTS

The weights and the data on the saturating qualities of the saturated felts, together with the physical properties of the saturants, are given in table 2.

[5] F. T. Carson and L. W. Snyder, *Increasing the capacity of the Elmendorf tearing tester*, Paper Trade J. 86, no. 13, 57-60 (March 29, 1928).

[6] Test is fully described in *The kerosene test for roofing felt*, P. W. Codwise, Paper Trade J. 87, no. 12, 60 (September 20, 1928).

TABLE 2.—*Composition of the saturated felts*

a	b	c	d
Sample	Weight, 108 sq. ft.	Saturation[1]	Actual saturation in terms of theoretical maximum
	lb	%	%
F1	31.3	163	80
F2	28.0	142	75
F3	31.3	147	74
F4	30.2	161	73
F5	32.5	177	73
F6	32.4	177	81
F7	31.3	165	79
F8	28.0	162	76
F9	29.2	174	80
F10	30.2	159	77
F11	30.2	177	77
F12	31.3	180	76
F13	31.3	179	77
B1	23.8	133	82
B2	25.9	156	83
B3	24.8	136	71
B4	24.8	144	87
B5	23.8	168	90
B6	24.8	179	82

SATURANT USED—ASPHALT

	F series	B series
Specific gravity at 77/77° F	1.035	1.001
Softening point (ring-and-ball) (° F)	114	113.5
Penetration at 77° F, 100 g, 5 sec (in 0.01 cm units)	121	143
Penetration at 32° F, 200 g, 60 sec (in 0.01 cm units)	35	64
Soluble in CS_2 (%)	99.8	99.5
Ductility at 77° F, 5 cm per minute (in cm units)	>100	48.3
Loss on heating—5 hours at 325° F (%)	.18	.07
Ash (%)	.23	.10

[1] Determined by analysis.

For convenience of comparison with the weathered samples, the results of the tensile-strength determinations and other data for these saturated felts are given in table 3.

Because of the different physical characteristics of the fibers used, the felts differed considerably in saturating capacities. To keep the saturation from exceeding 140 percent, as desired, was very difficult, of course, and was not always achieved, as table 2 shows. However, the saturation is fairly uniform when considered in terms of the maximum possible saturation, as indicated by the kerosene test. The ratio, obtained by dividing the percentage saturation by the maximum saturation (kerosene test), ranges from 73 to 81 percent. In this sense the felts were rather uniformly undersaturated, even though saturation of all the materials to the extent of 140 percent of the weight of the felts, as originally desired, was not accomplished.

TABLE 3.—*Test data on the saturated felts before and after exposure*

[The series of figures in the boxes indicate age of specimen, in years, when test was made]

a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t	u	v	w	x
Sample [1]	Wt of 108 sq. ft. [2]				Saturation				Tensile strength of strips 1 in. wide [3]						Tearing strength [3]						Water absorption (at 25° C for 24 hours)		
									Machine direction			Across machine direction			Machine direction			Across machine direction					
	0	1½	4	7	0	1½	4	7	0	1½	4	0	1½	4	0	1½	4	0	1½	4	0	1½	4
	lb	lb	lb	lb	%	%	%	%	lb	lb	lb	lb	lb	lb	g	g	g	g	g	g	%	%	%
F1	31	30	25	19	163	156	152	147	78	97	63	43	54	36	118	75	39	105	59	36	28	27	38
F2	28	27	24	19	142	140	137	129	86	86	58	46	49	33	116	63	35	95	46	30	35	29	38
F3	31	30	28	21	147	152	154	136	89	91	62	46	55	37	138	73	37	115	53	34	37	27	42
F4	30	30	27	21	161	168	161	144	70	82	55	40	47	35	111	63	35	96	48	28	30	26	38
F5	33	32	30	21	177	182	181	163	74	84	67	39	55	37	123	73	50	113	62	37	36	23	37
F6	32	31	27	18	177	173	175	159	70	83	58	39	51	35	119	62	40	97	55	31	34	22	34
F7	31	30	26	19	165	164	162	157	72	88	64	37	51	36	123	69	36	101	55	33	32	25	37
F8	28	26	22	16	162	163	150	131	72	74	52	36	44	29	99	51	31	85	41	24	37	25	42
F9	39	29	24	16	179	169	162	145	68	81	58	35	48	33	117	65	40	94	48	31	37	28	36
F10	30	29	23	20	159	167	156	149	72	87	66	39	51	34	121	72	39	97	51	30	43	23	46
F11	30	29	24	19	177	167	163	150	71	76	53	38	45	34	113	68	36	97	52	30	32	30	43
F12	31	30	25	20	180	192	171	167	60	75	54	34	48	30	139	66	37	109	53	31	36	32	44
F13	31	29	26	16	179	187	176	171	71	79	60	39	52	37	119	63	38	95	54	31	37	22	36
B1	24	22	22	19	133	112	97	78	63	44	34	46	35	23	75	44	30	65	41	25	13	19	29
B2	26	24	22	21	156	163	127	106	52	43	31	39	32	28	68	36	23	62	33	24	9	8	32
B3	25	24	21	19	136	153	119	99	58	40	27	44	32	24	35	24	14	38	25	16	12	14	38
B4	25	24	21	19	144	124	109	81	66	58	38	49	39	28	57	38	26	58	31	22	10	19	32
B5	24	22	18	19	168	139	126	107	60	52	33	51	40	32	56	35	24	52	37	23	13	25	41
B6	25	24	23	20	179	162	147	130	------	54	38	------	44	30	61	38	23	64	35	24	13	17	38

[1] The compositions of the felts corresponding to these numbers are given in table 1.

[2] The results are reported to the nearest whole number.

[3] The tensile- and tearing-strength tests were made under the standard atmospheric conditions of 65-percent relative humidity and 70° F. The results given are the average of 5 determinations. Strength tests were not made for the 7-year period, owing to the difficulty of obtaining suitable samples, nor did such tests seem necessary.

3. SMOOTH-SURFACED ROOFING

The finished roofings were all of the smooth-surfaced type, medium weight. As previously explained, they were made by saturating the dry felts and then coating both sides with a coating asphalt. The weights and the compositions of the roofings, together with the physical properties of the coating asphalts, are given in table 4.

TABLE 4.—*Composition of the smooth-surfaced roofings*

Sample	Weight 108 sq. ft. [1]	Contents per 108 sq ft, by analysis			
		Felt	Saturant	Coating	Surfacing
	lb	lb	lb	lb	lb
F1	62	10.8	19.8	27.6	3.4
F2	60	11.9	19.3	25.7	3.6
F3	62	12.2	17.0	28.7	3.9
F4	64	10.1	17.6	33.5	2.5
F5	59	13.0	16.3	26.1	4.0
F6	60	10.2	20.0	27.2	3.1
F7	63	12.2	21.0	26.3	3.1
F8	58	11.4	22.4	19.5	4.9
F9	55	10.6	19.3	18.6	3.6
F10	59	11.3	22.5	22.3	3.3
F11	62	11.7	22.7	24.8	2.5
F12	62	11.6	23.6	23.3	3.1
F13	57	11.1	23.1	19.1	3.9
B1	49	10.8	15.0	21.8	1.0
B2	46	11.4	19.2	14.8	1.0
B3	44	10.3	16.3	15.6	1.1
B4	42	10.2	14.1	17.4	.4
B5	43	9.3	15.8	16.8	1.3
B6	47	8.8	17.1	20.6	1.0

COATING USED—ASPHALT

	F series	B series
Specific gravity at 77/77° F	1.034	1.020
Softening point (ring-and-ball) (°F)	214	208
Penetration at 77° F, 100 g, 5 sec (in 0.01 cm units)	19.7	16
Penetration at 32° F, 200 g, 60 sec (in 0.01 cm units)	14.9	11
Penetration at 115° F, 50 g, 5 sec (in 0.01 cm units)	40.6	37
Soluble in CS_2 (%)	99.3	99.5
Ductility at 77° F, 5 cm per minute (in cm units)	4.1	4.3
Loss on heating 5 hours at 325° F (%)	.16	.02
Ash (%)	.48	.10

[1] These results are reported to the nearest whole number.

Additional data for the smooth-surfaced roofings were obtained, but for convenience of comparison with the weathered samples these are given in table 5.

TABLE 5.—*Test data on the smooth-surfaced roofings before and after exposure*

[The series of figures in the boxes indicate age of specimen, in years, when test was made]

a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t
Sample [1]	Wt of 108 sq ft [2]				Tensile strength of strips 1 in. wide [2]						Tearing strength [2]						Water absorption (at 25° F for 24 hours)		
					Machine direction			Across machine direction			Machine direction			Across machine direction					
	0	1½	4	7	0	1½	4	0	1½	4	0	1½	4	0	1½	4	0	1½	4
	lb	lb	lb	lb	lb	lb	lb	lb	lb	lb	g	g	g	g	g	g	%	%	%
F1	62	59	57	55	78	113	99	43	65	56	132	115	95	113	96	78	10	2	4
F2	60	50	60	44	94	123	114	52	67	66	140	90	95	106	83	80	9	1	5
F3	62	59	58	56	94	136	113	50	75	62	155	117	105	119	101	92	10	2	5
F4	64	60	60	58	81	123	104	46	70	67	147	113	103	128	98	93	10	0	4
F5	59	58	57	54	86	123	107	49	73	70	181	120	103	118	105	94	10	2	4
F6	60	59	57	57	80	113	95	46	69	61	139	83	97	114	82	83	9	1	3
F7	63	60	58	58	80	124	107	44	70	64	151	110	101	115	102	90	10	1	4
F8	58	57	56	54	81	117	104	47	64	62	131	103	94	110	100	86	5	0	3
F9	55	54	53	48	80	117	108	45	71	62	135	97	95	93	93	78	11	3	6
F10	59	55	58	43	83	120	106	45	70	62	152	102	103	114	94	89	10	0	4
F11	62	59	58	56	76	127	107	42	68	62	159	114	97	117	93	83	11	1	5
F12	62	59	57	55	76	118	102	42	65	56	166	113	102	114	93	83	9	0	4
F13	57	57	55	52	84	121	99	45	70	58	141	105	99	103	96	81	7	2	4
B1	49	45	46	47	78	106	93	58	82	66	91	63	60	90	59	64	2	3	2
B2	46	44	42	46	64	83	72	48	66	52	59	40	42	58	37	41	1	2	2
B3	44	40	39	37	62	73	63	50	56	55	39	35	38	44	35	38	0	1	7
B4	42	44	40	34	75	100	94	56	73	73	55	48	51	60	48	52	2	1	2
B5	43	39	42	44	70	83	84	63	72	73	61	51	42	58	48	46	0	0	2
B6	47	45	42	42	65	95	86	52	79	75	70	53	54	72	54	56	0	3	2

[1] The compositions of the felts corresponding to these numbers are given in table 1.
[2] The results are reported to the nearest whole number.
[3] The tensile- and tearing-strength tests were made under the standard atmospheric conditions of 65-percent relative humidity and 70° F. The results are the average of 5 determinations.

V. MEASUREMENTS ON MATERIALS AFTER EXPOSURE

As previously stated, samples of the saturated felts and of the smooth-surfaced roofing were exposed on racks to outdoor weathering (fig. 1). At certain intervals, namely, after exposure for 1½, 3½, 4, and 7 years, sets of the specimens were removed from the racks and tested. The results of the tests for the 3½ years of exposure are, however, not recorded in this paper, since they did not vary much from those of the 4-year period. The tables show the weights, the saturations, the tensile and tearing strengths, and the capacities for absorption of water of the saturated felts before and after exposure to the weather. Corresponding data for the smooth-surfaced roofings are also shown. As the tables show, not all the tests were made for the 7-year period, owing to the difficulty of obtaining suitable samples. However, tables 6, 7, 8, and 9 list some special determinations on the materials after 7 years of exposure.

1. SATURATED FELTS

Table 3 shows the weights of the saturated felts before and after exposure. In table 6, column g, the percentage losses in weight for the 7 years of exposure have been calculated for the saturated felts. In column d the weights are given for the desaturated (extracted)

felts, while in column e the percentage losses are given. For these latter figures the weathered saturated felts were treated with carbon tetrachloride to remove the asphalt.

The saturated felts of the F series show an increase in tensile strength in both directions (table 3) up to about 2 years of exposure, owing to hardening of the asphalt, and thereafter show a constant decrease in strength. The B series of saturated felts show a decrease in strength after weathering for 1½ years. All tearing tests show a decrease in resistance to tearing after 1½ years of exposure.

TABLE 6.—*Composition of saturated felts before and after 7 years of exposure*

a	b	c	d	e	f	g	h	i	j	k
Sample	Weight per 108 sq ft			Change in weight of desaturated felt due to exposure for 7 years [2]	Wt of saturated felt after 7 years of exposure	Loss in weight of saturated felt due to exposure for 7 years	Composition of saturated felt before exposure. By analysis		Composition of saturated felt after weathering 7 years	
	Original dry felt	Original saturated felt before exposure	Desaturated felt after 7 years' exposure [1]				Felt	Saturant	Felt	Saturant
	lb	lb	lb	%	lb	%	%	%	%	%
F1	11.0	31.3	7.6	−31	18.8	40	38	62	40	60
F2	11.2	28.0	8.2	−27	18.8	33	41	59	44	56
F3	12.3	31.3	8.7	−29	20.5	35	40	60	42	58
F4	12.6	30.2	8.4	−33	20.5	32	38	62	41	59
F5	12.1	33.5	8.0	−34	21.0	37	36	64	38	62
F6	11.4	32.4	7.0	−39	18.1	44	36	64	39	61
F7	11.4	31.3	7.2	−37	18.5	41	38	62	39	61
F8	10.3	28.0	6.8	−34	15.7	44	38	62	43	57
F9	11.4	29.2	6.7	−41	16.4	44	36	64	41	59
F10	10.8	30.2	8.0	−26	19.9	34	39	61	40	60
F11	11.0	30.2	7.6	−31	19.0	37	36	64	40	60
F12	10.8	31.3	7.6	−30	20.3	35	36	64	37	63
F13	10.5	31.3	5.9	−44	16.0	49	36	64	37	63
B1	9.8	23.8	10.5	+7	18.7	21	43	57	56	44
B2	10.0	25.9	10.0	0	20.6	20	39	61	49	51
B3	9.9	24.8	9.7	−2	19.3	22	42	58	50	50
B4	9.0	24.8	10.5	+17	19.0	23	41	59	55	45
B5	9.1	23.8	9.1	0	18.8	21	37	63	48	52
B6	9.3	24.8	8.6	−8	19.8	20	36	64	43	57

[1] Obtained by extracting the exposed saturated felt samples with carbon tetrachloride. Seven strips (each 2 by 5 in.) of each material were extracted and the results are the average of these 7 strips.

[2] The causes of the increases in weight (+) shown by some of the samples are not known. The figures, however, do show that the felts in the F series have deteriorated considerably more than those of the B series.

The amounts of water absorbed by the materials before and after exposure are shown in table 3. These determinations were made by immersing the samples in water at 25° C for 24 hours and then determining the percentage increase in weight based on the weight of the original dry material.[7]

It will be noted from table 3 that the ratio of asphalt to felt (percentage saturation) decreased on exposure, and more so for the B series than the F series. The difference between the changes in ratio is explained by the fact that the more compact felts of the B series lost less material by exfoliation than the F series. Exfoliation takes

[7] See footnote 3.

place on the surface of the saturated felt and thus causes the felt fibers and asphalt to disappear simultaneously. In the case of the B felts, however, the fiber portion, owing to the compactness of the felts as previously described, did not disappear as rapidly as the asphalt portion and so the fiber or felt became larger in proportion to the asphalt and this accounts for the more rapid decrease in percentage of saturation in the B series of felts. This behavior is further illustrated by the data in columns h, i, j, k (table 6), which show the composition of the saturated felts before and after exposure; in column d, which shows the weights of the desaturated felts; and in columns g and e, which show losses in weight of the saturated and desaturated felts after exposure for 7 years. The data on thicknesses in table 7 further show the degree of exfoliation in the saturated felts, particularly the data given in column d.

TABLE 7.—*Change in thickness of saturated felts during exposure*

a	b	c	d	e	f	g
Sample	Thickness of original dry felt [1]	Thickness of saturated felt after desaturation (exposed 7 years)	Thickness loss in the desaturated felts	Thickness of original saturated felt before exposure	Thickness of saturated felt before desaturation (exposed 7 years)	Thickness change in saturated felts due to exposure for 7 years
	in.	in.	%	in.	in.	%
F1	0.053	0.038	28	0.057	0.052	−9
F2	.053	.042	21	.053	.051	−4
F3	.062	.040	35	.061	.054	−11
F4	.067	.041	39	.058	.053	−9
F5	.068	.040	41	.065	.054	−17
F6	.063	.035	44	.060	.051	−15
F7	.059	.036	39	.059	.054	−8
F8	.054	.032	41	.053	.046	−13
F9	.058	.031	47	.055	.051	−7
F10	.057	.036	37	.057	.053	−7
F11	.060	.037	38	.057	.057	0
F12	.058	.039	33	.063	.060	−5
F13	.059	.032	46	.062	.046	−26
B1	.042	.038	10	.044	.047	+6
B2	.050	.043	14	.052	.052	0
B3	.054	.045	17	.057	.052	−9
B4	.041	.041	0	.048	.048	0
B5	.045	.040	11	.046	.047	+2
B6	.049	.038	22	.049	.046	−6

[1] Felt saturated with asphalt and then extracted with carbon tetrachloride does not change in thickness.

All these data on weights, strength, and similar tests show that the individual saturated felts of the F series have weathered to approximately the same degree. Moreover, their appearance after weathering is similar. The conclusion is, therefore, drawn that all felts of the F series are about equally durable. Similarly, all saturated felts of the B series are equally durable, but the F series has deteriorated considerably more than the B series because of a greater degree of exfoliation.

2. SMOOTH-SURFACED ROOFINGS

Corresponding data for the smooth-surfaced roofings are found in tables 5, 8, and 9. In particular, the data show that the asphalt coating protected the saturated felts from weathering. Upon extracting the asphalt with carbon tetrachloride the felts showed relatively little change from their original condition. The smooth-surfaced roofings showed no marked differences in weathering in the F and B series, although the appearance was slightly in favor of the B series.

TABLE 8.—*Composition of smooth-surfaced roofings before and after 7 years of exposure*

a	b	c	d	e	f	g
Sample	Wt. per 108 sq. ft.			Change in weight of desaturated felt due to exposure for 7 years [2]	Weight per 108 sq ft of smooth-surfaced roofing after 7 years, exposure	Change in weight of smooth-surfaced roofing due to exposure for 7 years
	Original dry felt	Original smooth-surfaced roofing before exposure	Desaturated felt after 7 years' exposure [1]			
	lb	lb	lb	%	lb	%
F1	11.0	61.5	10.5	−5	55.3	−10
F2	11.2	60.4	10.9	−3	44.4	−26
F3	12.3	61.5	11.2	−9	56.1	−9
F4	12.6	63.7	12.7	+1	58.2	−9
F5	12.1	59.4	12.6	+4	54.4	−8
F6	11.4	60.4	10.9	−4	56.7	−6
F7	11.4	62.6	11.4	0	57.8	−8
F8	10.3	58.3	8.6	−17	54.0	−7
F9	11.4	55.0	10.3	−10	48.3	−13
F10	10.8	59.4	10.8	0	43.2	−27
F11	11.0	61.5	10.8	−2	56.2	−9
F12	10.8	61.5	10.8	0	55.3	−10
F13	10.5	57.2	9.9	−6	51.9	−9
B1	9.8	48.6	10.8	+10	47.3	−3
B2	10.0	46.4	11.4	+14	45.8	−1
B3	9.9	44.2	10.4	+5	37.4	−15
B4	9.0	42.1	11.1	+23	33.7	−18
B5	9.1	43.2	9.4	+3	44.2	+2
B6	9.3	47.5	8.5	−9	42.4	−11

[1] Obtained by extracting the weathered samples of smooth-surfaced roofing with carbon tetrachloride. Seven strips (each 2 by 5 in.) of each material were extracted and the results given are the average for these 7 strips.

[2] The causes of the increases in weight (+) shown by some of the samples are not known.

TABLE 9.—*Change in thickness of smooth roofings during exposure*

Sample	a	b	c	d	e	f
	Thickness of original dry felt	Thickness of roofing after desaturation. Exposed 7 years	Thickness change in the desaturated roofing	Thickness of original roofing	Thickness of roofing before desaturation. Exposed 7 years	Thickness change in the roofing due to exposure 7 years *
	in.	in.	%	in.	in.	%
F1	0.053	0.051	−4	0.105	0.116	+9
F2	.053	.050	−6	.104	.111	+6
F3	.062	.055	−11	.105	.119	+12
F4	.067	.063	−6	.109	.112	+3
F5	.068	.066	−3	.104	.105	+1
F6	.063	.056	−11	.108	.110	+2
F7	.059	.061	+3	.107	.106	−1
F8	.054	.051	−6	.097	.103	+6
F9	.058	.052	−10	.092	.098	+6
F10	.057	.055	−4	.099	.090	−9
F11	.060	.055	−8	.104	.112	+7
F12	.058	.057	−2	.106	.118	+10
F13	.059	.054	−8	.094	.110	+15
B1	.042	.044	+5	.086	.090	+44
B2	.050	.051	+2	.087	.087	0
B3	.054	.053	−2	.088	.084	−5
B4	.041	.049	+20	.074	.072	−3
B5	.045	.047	+4	.085	.090	+6
B6	.049	.043	−12	.090	.092	+2

* These thickness data are inaccurate owing to blister formations in the smooth-surfaced roofing which exaggerate the thickness measurements.

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